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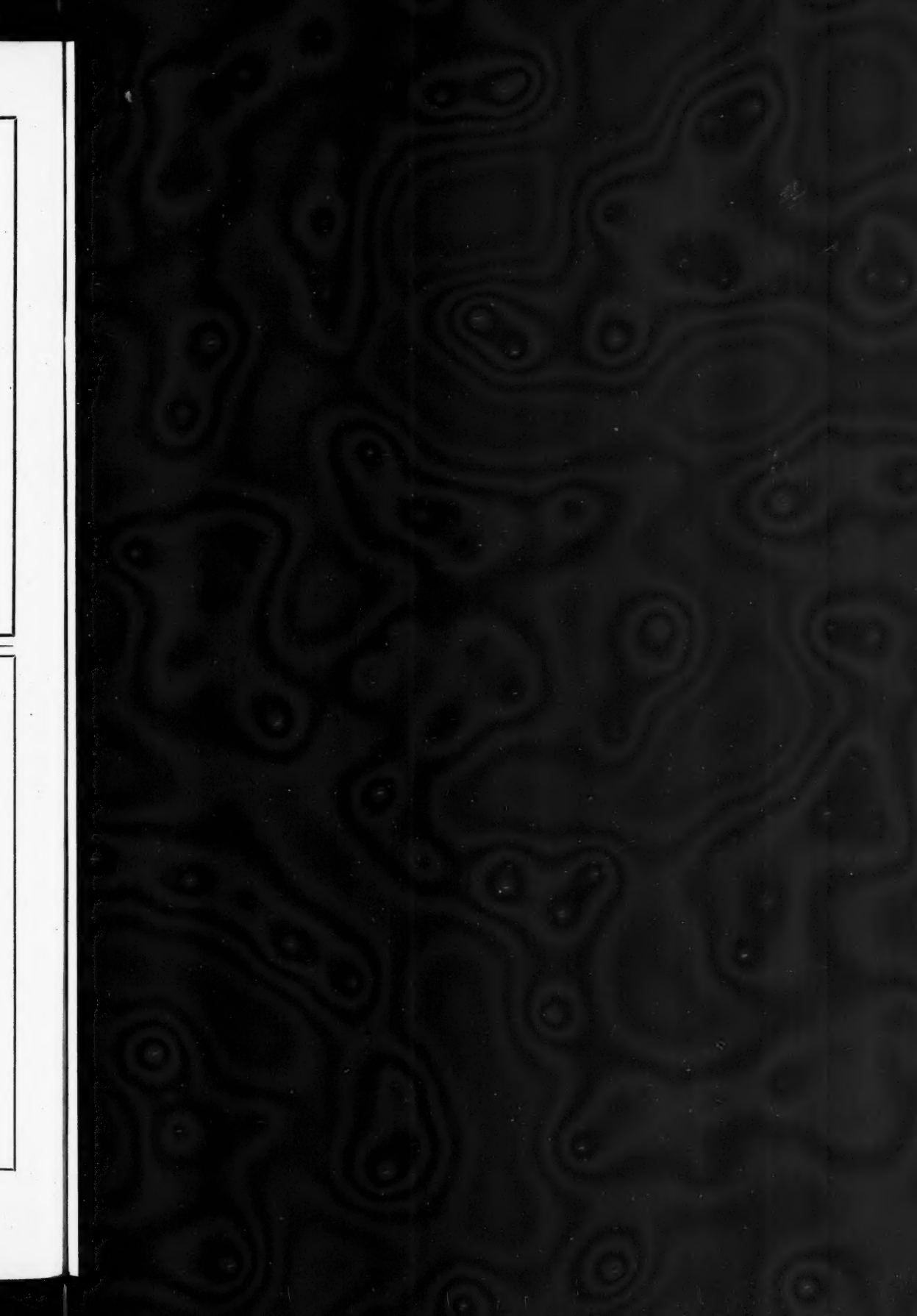
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## THE CLARK HYDROGEN-ELECTRODE VESSEL AND SOIL MEASUREMENTS

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In certain soil studies specific chemical reaction must be accurately determined, and it is most accurately determined by measurement of the hydrogen-ion concentration.

Two methods are available for the measurement of hydrogen-ion concentration in soils—the colorimetric and the electrometric. The colorimetric method requires the use of soil extracts and color indicators of chemical reaction. Such indicators ionize, with production or change of color, in solutions containing definite hydrogen-ion concentrations. Wherry (1) has used a series of such indicators to determine the hydrogen-ion concentrations of soil extracts at various points between superacid and superalkaline soils. While such a method is more accurate than the older titration methods, yet it indicates the specific reaction of the soil indirectly.

The hydrogen ion carries a positive electric charge, thus maintaining an electric potential in the soil solution. The electrometric method measures this potential by means of a potentiometer and galvanometer; the electric potential in the soil solution being balanced against a known resistance, the accuracy of such measurements depending upon the stability of this balance. Gillespie and Hurst (2) have devised a hydrogen-electrode vessel for soil measurements which very nearly yields a steady potential balance. Using the Clark hydrogen-electrode vessel we obtained a steady potential balance and satisfactory electrometric measurements of specific soil reactions.

In field studies and in studies of processes constant over a wide range of hydrogen-ion concentrations, an approximate determination is sufficient, and the colorimetric method may be used. In more particular studies and when processes may be seriously affected by the hydrogen-ion concentration of the solution, the electrometric method should be used because it is the most accurate method available.

The apparatus used in this investigation consisted of the Clark hydrogen-ion apparatus supplied by the Leeds and Northrup Company, a portable lamp and scale galvanometer, a Leeds and Northrup type K potentiometer and a standard Weston cell, Model 4. Two Columbia dry cells furnished the working current. Hydrogen obtained from a Kipps' generator was passed through two wash bottles (the first containing 0.5 *N* NaOH and a small quantity of lead

acetate; the second containing distilled water) and then conducted into the hydrogen-electrode vessel. A normal KCl calomel electrode was used and normal KCl solution, saturated with calomel, was used in the connecting vessel. Measurements were made at room temperature without the aid of a constant temperature bath, but the temperature of the calomel electrode was carefully noted immediately following each measurement, the reading being made to the nearest degree or half-degree Centigrade. Following Clark's suggestions, hydrogen was not bubbled through the sample under measurement. Clark (3) states that "in fluids containing carbonate the double effect of the  $\text{CO}_2$  upon the partial pressure of hydrogen and upon the hydrogen-ion equilibrium renders accurate measurements difficult. It is of more importance to maintain the original  $\text{CO}_2$  content of the solution than it is to be concerned about the effect of  $\text{CO}_2$  upon the partial pressure of hydrogen." The platinum electrodes were coated with platinum black at intervals of four to seven weeks and kept in distilled water during the intervals; they were saturated with hydrogen immediately before each day's series of measurements.

To test the accuracy of the electrometric measurements made by such an apparatus under the above conditions, a 0.1 *N* HCl solution was measured with the results shown in table 1.

TABLE 1

	TIME	READING	TEMPERATURE	pH VALUE	THEORY	
		volts	°C.			
0.1 N HCl, factor 1.0006.....	10.20	0.3490	31	1.06	} 1.07 (4)	
	10.22	0.3490				
Duplicate.....	10.37	0.3475	31	1.08		
	10.39	0.3475				

As a further test two standard "buffer" solutions were measured electrometrically and colorimetrically. Results are given in table 2.

The colorimetric method measures to two-tenths of a pH value. Tables 1 and 2 demonstrate that without extensive equipment electrometric measurements of hydrogen-ion concentrations afford a fair degree of accuracy. Great refinement in correcting for barometric and temperature fluctuations is necessary only in physio-chemical research.

In making the soil measurements the hydrogen-electrode vessel was half filled with  $\text{CO}_2$ -free distilled water, a small portion of water entering the reservoir; 4 gm. of air-dried, or 5 gm. of fresh soil were introduced in small portions into the vessel, carefully mixing the soil and water; the vessel was completely filled with  $\text{CO}_2$ -free distilled water, the platinum electrode carefully inserted, avoiding the formation of air bubbles; the stopcocks closed, and the vessel placed in an inverted position in the shaking apparatus and connected with the hydrogen generator in the usual manner. In this inverted position

the soil settles upon the upper surface of the vessel making it possible to sweep out the water with hydrogen. As much water as possible was swept out with

TABLE 2

	TIME	READING	TEMPERATURE	ELECTRO-METRIC pH VALUE	COLORIMETRIC pH VALUE
		<i>volts</i>	<i>°C.</i>		
Buffer solution 1.....	2.17	0.6995	32	6.88	7.0
	2.19	0.6995			
Duplicate.....	2.43	0.6995	32	6.88	7.0
	2.45	0.6995			
Buffer solution 2.....	3.06	0.7670	32	7.99	8.2
	3.08	0.7670			
Duplicate.....	3.26	0.7675	32	8.00	8.2
	3.28	0.7675			

TABLE 3

	ELECTRODE VESSEL	TIME	READING	TEMPERA- TURE	pH VALUE
			volts	°C.	
Silt loam, 20.....	1	10.56	0.7235	21.0	7.50
		10.58	0.7235		
	1	11.10	0.7420	25.0	7.55
		11.12	0.7420		
	1	11.46	0.7290	20.5	7.61
		11.48	0.7290		
Average .....					7.55
Silt loam, 20.....	2	12.21	0.7270	25.0	7.48
		12.23	0.7270		
	2	12.33	0.7340	20.5	7.69
		12.35	0.7340		
	2	3.41	0.7385	20.5	7.77
		3.43	0.7385		
	2	4.25	0.7240	20.5	7.53
		4.27	0.7240		
Average .....					7.62

hydrogen, the stopcocks closed, the vessel disconnected and removed from the shaking apparatus. The vessel was now shaken by hand for 5 minutes, then

placed in the proper position in the shaking apparatus and so adjusted that the platinum electrode was completely submerged in the wet soil. After three minutes the vessel was so re-adjusted that the platinum electrode was half immersed in the wet soil, and the connections were made with the potentiometer, the apparatus remaining undisturbed for six minutes, after which the readings were made.

To test the accuracy of such electrometric measurements different hydrogen-electrode vessels and different platinum electrodes were used to measure the same soil. Results are shown in table 3.

Having established a fair degree of accuracy for the electrometric measurements, six samples of fresh soils from the Station farm were measured as in table 4.

TABLE 4  
*Fresh soils*

	READING	TEMPERATURE	pH VALUE	AVERAGE
	<i>volts</i>	<i>°C.</i>		<i>pH</i>
Silt loam, 1. 26.6 per cent H <sub>2</sub> O.....	0.6000	19.0	5.41	} 5.31
Duplicate.....	0.5890	19.0	5.22	
Silt loam, 2. 26.6 per cent H <sub>2</sub> O.....	0.6020	19.0	5.45	} 5.46
Duplicate.....	0.6050	20.0	5.48	
Silt loam, 3. 25 per cent H <sub>2</sub> O.....	0.5940	19.5	5.30	} 5.43
Duplicate.....	0.6100	20.0	5.57	
Silt loam, 4. 25 per cent H <sub>2</sub> O.....	0.5880	20.0	5.19	} 5.37
Duplicate.....	0.6090	20.0	5.55	
Silt loam, 5. 25 per cent H <sub>2</sub> O.....	0.6100	22.0	5.54	} 5.69
Duplicate.....	0.6280	22.0	5.85	
Silt loam, 6. 25 per cent H <sub>2</sub> O.....	0.6180	21.5	5.51	} 5.66
Duplicate.....	0.6250	21.5	5.81	

The same samples of soil were air-dried, passed through a 1 mm. sieve, stored in Mason jars on the laboratory table for 12 weeks and then remeasured as in table 5.

These air-dried soils, together with a strongly acid soil (silt loam, 17), were measured colorimetrically using Wherry's method. The results are tabulated together with their electrometric measurements in table 6.

Hopkins test showed a lime requirement of 108 pounds of calcium carbonate for soils 1, 2 and 4; 140 pounds for soil 3; 36 pounds for soils 5 and 6; and 1786 pounds for soil 17. Soils 1 to 6 are similar in character and highly phosphatic; soil 17 is of a different type and moderately phosphatic.

TABLE 5  
*Soils after air-drying*

	READING	TEMPERATURE	pH VALUE	AVERAGE pH VALUE	
				Air-dried	When fresh
	<i>volts</i>	<i>°C.</i>			
Silt loam, 1 .....	0.5970	31.5	5.19	5.23	5.31
Duplicate.....	0.6030	32.0	5.28		
Silt loam, 2 .....	0.6030	31.5	5.29	5.09	5.46
Duplicate.....	0.5790	31.5	4.89		
Silt loam, 3 .....	0.5840	30.5	4.98	4.98	5.43
Duplicate.....	0.5840	31.0	4.98		
Silt loam, 4 .....	0.5730	31.0	4.80	5.02	5.37
Duplicate.....	0.6010	31.5	5.25		
Silt loam, 5 .....	0.6190	32.0	5.54	5.52	5.69
Duplicate.....	0.6165	31.5	5.51		
Silt loam, 6 .....	0.6000	30.0	5.26	5.37	5.66
Duplicate.....	0.6140	30.0	5.49		

TABLE 6

SOIL	SPECIFIC REACTION	pH VALUE	
		Colorimetric	Electrometric
	<i>acid</i>		
1	3+	6.6	5.23
2	3+	6.6	5.09
3	3+	6.6	4.98
4	3+	6.8	5.02
5	3+	6.5	5.52
6	3+	6.6	5.37
17	10	6.0	3.44

## SUMMARY

The hydrogen-ion concentration of the fresh and of the air-dried soils studied may be measured directly by using the Clark hydrogen-electrode vessel.

The air-dried soils measured in this manner show a slightly greater hydrogen-ion concentration than they do when measured in a fresh condition, and a distinctly greater hydrogen-ion concentration than they do when measured by Wherry's method.

It has been shown that without extensive equipment electrometric measurements of hydrogen-ion concentrations in these soils afford a fair degree of accuracy.

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# MICROORGANISMS CONCERNED IN THE OXIDATION OF SULFUR IN THE SOIL: III. MEDIA USED FOR THE ISOLATION OF SULFUR BACTERIA FROM THE SOIL<sup>1</sup>

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It has been known for a long time that sulfur and its compounds can be oxidized by various groups of bacteria, and in this process the sulfur is used, in place of carbon compounds, as a source of energy. The carbon necessary for the building up of the protoplasm of the organisms is obtained either from carbonates or from the CO<sub>2</sub> of the atmosphere. The various microorganisms concerned in the oxidation of sulfur and sulfur compounds are all brought together into one large group, under the name of sulfur bacteria. However, the fact that these organisms vary greatly both in their morphology and metabolism has led various investigators to subdivide them into several groups. The earlier investigations of Winogradsky (17) and other investigators on Beggiatoa, Thiobacillus, purple bacteria, etc., used, primarily, hydrogen sulfide and sulfides as a source of sulfur. These substances are presumably oxidized first to sulfur and then to sulfuric acid. The organisms were grouped together by Omelianski under "sulfur" bacteria. They are usually subdivided as by Omelianski (12) and Dügge (2) as follows:

1. Thread forming, colorless bacteria, accumulating sulfur within their cells.
2. Non-thread forming, colorless bacteria, accumulating sulfur within their cells.
3. Purple bacteria.

As a result of the work of Nathanson in 1902 (11), Beijerinck (1) and Jacobson (5, 6), on the oxidation of thiosulfate, a new group of organisms was described. These bacteria are colorless, non-thread forming, and use thiosulfate as a source of energy; they do not accumulate any sulfur within their cells but produce an abundance of sulfur outside of their cells. These bacteria were naturally placed in a fourth and new group under the name of "thiosulfate" bacteria, or, according to Omelianski (12), "thionic acid" bacteria.

Recently a fifth group of sulfur bacteria has been added. This includes the organism which is concerned in the oxidation of elementary sulfur in the so-called "sulfur-floats-soil" composts, developed by Lipman (8), McLean (10) and their associates. This organism isolated by the author and associates

<sup>1</sup> Paper No. 59 of the Journal series, New Jersey Agricultural Experiment Stations, Department of Soil Chemistry and Bacteriology.



(9, 14, 15, 16) is able to oxidize elementary sulfur very rapidly to sulfuric acid. It is a small, colorless, non-thread forming organism, using primarily elementary sulfur as a source of energy, not accumulating any sulfur within or without its cells. This organism (*Thiobacillus thiooxidans*) can be readily isolated in pure culture, by the use of proper media, and can be kept in culture more readily than most of the sulfur organisms studied so far.

The classification of the organisms concerned in the oxidation of sulfur into I, sulfur bacteria, including the first 3 groups, and II, thionic acid bacteria, including group 4, might be modified in view of the discovery of *Thiobacillus thiooxidans*. This modification would consist in dividing the sulfur bacteria, if physiological characteristics are taken as a basis of subdivision, into 3 large groups: I. "Sulfide" bacteria, which would take the place of Omelianski's "sulfur" bacteria. Into this group we would include organisms which oxidize primarily  $H_2S$  and sulfides, with the accumulation of sulfur within the cells of the organisms. The first three smaller groups (arabic numerals) would be included into this large group (I). II. "Thiosulfate" or "thionic acid" bacteria, which oxidize primarily thiosulfates, to some extent sulfides and elementary sulfur with the accumulation of sulfur outside of their cells and the transformation of sulfur compounds into sulfates and persulfates. This group would include the small group, no. 4, which is the same as Omelianski's second group. III. "Sulfur" bacteria proper, organisms which oxidize primarily elementary sulfur, without accumulating any sulfur within or without the cells, but with the production of large amounts of acid formed by the oxidation of sulfur. This large group would include organisms like those studied by the author and associates (group 5).

From the systematic point of view, the members of group I (1, 2, 3) belong partly to the *Thiobacteriales*, partly to other groups, while groups II and III (4, 5) belong to one genus *Thiobacillus* closely related to the other autotrophic bacteria among the *Eubacteriales*.

However, this new system would not present greater advantages over the old in view of the fact that organisms belonging to group II can also oxidize elementary sulfur, and organisms in group III can also use, to a small extent, sulfides and thiosulfates.

The subdivision of the organisms concerned in the oxidation of sulfur and its compounds directly into the minor five groups gives a good working basis. Of these five groups only 4 and 5 are found in the soil or may become active there in oxidizing sulfur; the studies presented in this as well as in the following papers will be limited to these 2 groups. Group 1 (*Beggiatoa*, etc.) has so far not been demonstrated in normal, cultivated soils. This is also true of the purple bacteria,—it is not even definitely established, as far as pure cultures are concerned, that these organisms are able to oxidize sulfur compounds. Representatives of group 2 have been mentioned as soil organisms by Gicklehorn (4), but the work of this investigator consisting merely in examining microscopically impure cultures, without any attempt to a study of pure cultures and

physiological activities, deserves little consideration. Groups 4 and 5, the first studied by Nathanson (11), Beijerinck (17), Jacobsen (5, 6), Lieske (7), Gehring (3), and Trautwein (13), the second by the author and associates (9, 14, 15, 16), deserve careful consideration as soil microorganisms.

So far, three species belonging to these 2 groups have been described: *Thiobacillus thioparus* Beijerinck, *Thiobacillus denitrificans* Beijerinck, and *Thiobacillus thiooxidans* Waksman and Joffe. All these three organisms are autotrophic deriving their carbon from  $\text{CO}_2$ ; however, the form related to *Th. denitrificans* isolated by Trautwein can also thrive on organic carbon compounds. *Th. thioparus* and *Th. denitrificans* were placed in group 4 and *Th. thiooxidans* in group 5. The differentiating characters between these two groups can be summarized under the following headings:

A. The organisms placed in group 4 were isolated by the use of thiosulfate as a source of sulfur, although they are also able to oxidize  $\text{H}_2\text{S}$ , sulfides and even elementary sulfur. *Thiobacillus thiooxidans* was isolated by the use of elementary sulfur (powdered); it oxidizes thiosulfate and sulfides only to a small extent.

B. The *Th. thioparus* and *Th. denitrificans* produce free sulfur outside of their cells in the form of a pellicle. Trautwein (13) recently described an organism related to *Th. denitrificans*, but which grows aerobically and does not accumulate any sulfur. *T. thiooxidans* does not produce any sulfur from thiosulfate, which is rapidly oxidized to sulfuric acid.

C. *Th. thioparus* and *Th. denitrificans* are according to Beijerinck (1)  $3 \times 0.5 - 1 \mu$  in size, motile, and can be cultivated on agar media. The denitrifying sulfur oxidizing organisms studied by Lieske and Gehring are only  $1 \mu$  long. The organism studied by Trautwein is  $1-2 \times 0.5 \mu$ , motile and reduces nitrates, under anaerobic conditions. *Th. thiooxidans* is  $0.75-1 \times 0.5 \mu$ , non-motile, was not cultivated so far on solid media.

D. The organisms belonging to group 4 oxidize the thiosulfate to sulfate and persulfate, according to Nathanson (11) and Trautwein (13), while the *Th. thiooxidans* oxidizes thiosulfate to sulfate, which will explain the following difference.

E. The optimum and limiting reactions of *Th. thioparus* and *Th. denitrificans* have not been stated, but, from the work of Trautwein, we find that his organism, closely related to the other two forms, has its optimum reaction in the alkaline range ( $\text{pH} = 8.0$ ), and, when grown on slightly acid media, changes the reaction to alkaline. *Th. thiooxidans* grows in a distinctly acid reaction (optimum  $\text{pH} = 3.0$ ) and produces large amounts of acid. The fact that Jacobsen (6) obtained active oxidation of sulfur by means of an organism which was supposed to be the same as Beijerinck's form, would lead to think that he might have had, in addition to that organism, also *Th. thiooxidans* or a closely related strain.

As a matter of fact, this last factor, namely, the question of reaction, could in itself be used as a physiological characteristic for the classification of sulfur bacteria. It would place the optimum activity of the first four groups on the alkaline or neutral side and group 5 on the far acid side.

According to the work carried on at the New Jersey Experiment Stations (9, 16), *Th. thiooxidans* seems to be a distinct species, as far as both morphological and physiological activities are concerned. The other two organisms vary somewhat in their description by the different investigators. Beijerinck (1) stated that *Th. thioparus* is practically undifferentiated morphologically from *Th. denitrificans*. These two organisms were supposed to be about  $3 \mu$  long and  $0.5$  to  $1 \mu$  in diameter; but Lieske and Gehring found *Th. denitrifi-*

*cans* only  $1\mu$  long and Duggeli (2) states that *Th. thioparus* is only 0.3–0.5 $\mu$  long. While Beijerinck found that his organisms separated sulfur from thio-sulfate, Trautwein made a detailed study of a denitrifying organism which is unable to do that. This would simply indicate the fact that various organisms have been studied by various investigators and that we have here more than two organisms. A more detailed comparative study of the various organisms representing these groups is needed. This is also substantiated by the results obtained in our own laboratory on bacteria which oxidize sulfur under alkaline conditions and which will be published in the following paper.

Another important differentiating point between *Th. thiooxidans* and the other two organisms is their viability. The first organism has been kept in pure culture, in liquid media, for over a year, without losing either viability or physiological characteristics; the *Th. thioparus* and *Th. denitrificans* have been reported by Beijerinck (1), Gehring (5) and others to deteriorate rapidly in pure culture. The organism studied by Trautwein (13) can be cultivated in ordinary bouillon and can be kept alive in that medium for many months, without losing its power of sulfur oxidation.

As to the occurrence of these organisms in the soil, Gehring (5) stated that the denitrifying sulfur oxidizing bacteria are present in various soil types, but different soils contain different races of this organism which differ greatly in virulence. Trautwein (13) demonstrated the presence of his organism in the soil, while *Th. thiooxidans* has been isolated by Waksman and Joffe (16) from soil-sulfur composts and was used by Lipman (8) in the inoculation of elementary sulfur for application to soils.

As a result of these comparisons, we find these different forms of sulfur oxidizing organisms and others which will, no doubt, be added to the list require various cultural treatment and methods of study.

The various media used for the isolation of the sulfur oxidizing organisms that are or may become active in the soil, are as follows:

#### 1. Beijerinck (1) medium

Tap water.....	1000 cc.	NH <sub>4</sub> Cl.....	0.1 gm.
Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> .....	5.0 gm.	NaHCO <sub>3</sub> .....	1.0 gm.
MgCl <sub>2</sub> .....	0.1 gm.	Medium unsterilized.	
Na <sub>2</sub> HPO <sub>4</sub> .....	0.2 gm.		

#### 2. Jacobsen (5) medium

Distilled water.....	1000 cc.	MgCl <sub>2</sub> .....	0.2 gm.
K <sub>2</sub> HPO <sub>4</sub> .....	0.5 gm.	CaCO <sub>3</sub> or MgCO <sub>3</sub> .....	20.0 gm.
NH <sub>4</sub> Cl.....	0.5 gm.	Precipitated sulfur.....	10.0 gm.

#### 3. Lieske (7) medium

Distilled water.....	1000 cc.	KNO <sub>3</sub> .....	5.0 gm.
Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> .....	5.0 gm.	NaHCO <sub>3</sub> .....	1.0 gm.
MgCl <sub>2</sub> .....	0.1 gm.	CaCl <sub>2</sub> , FCl <sub>2</sub> .....	Traces.
K <sub>2</sub> HPO <sub>4</sub> .....	0.2 gm.		

## 4. Trautwein (13) medium

Distilled water	1000 cc.	KNO <sub>3</sub>	1.0 gm.
Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub>	2.0 gm.	NH <sub>4</sub> Cl	0.1 gm.
MgCl <sub>2</sub>	0.1 gm.	NaHCO <sub>3</sub>	1.0 gm.
Na <sub>2</sub> HPO <sub>4</sub>	0.2 gm.		

5. Medium used by author and associates (9)<sup>2</sup>

Distilled water	1000 cc.	MgSO <sub>4</sub> ·7H <sub>2</sub> O	0.5 gm.
(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	2.0 gm.	FeSO <sub>4</sub>	0.01 gm.
K <sub>2</sub> HPO <sub>4</sub>	1.0 gm.	Sulfur	10.0 gm.
KCl	0.5 gm.	Ca <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub>	10.0 gm.

6. Modification of medium 5 for *Th. thiooxidans*<sup>3</sup>  
(pH value about 4.0)

Distilled water	1000 cc.	FeSO <sub>4</sub>	Trace
(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	0.2 gm.	KH <sub>2</sub> PO <sub>4</sub>	3.0 gm.
MgSO <sub>4</sub> ·7H <sub>2</sub> O	0.5 gm.	Sulfur	10.0 gm.
CaCl <sub>2</sub>	0.25 gm.		

7. Second modification of medium 5<sup>3</sup>  
(pH value about 3.0)

(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	0.2 gm.	Sulfur	10.0 gm.
MgSO <sub>4</sub> ·7H <sub>2</sub> O	0.5 gm.	KH <sub>2</sub> PO <sub>4</sub> , 1.0 M solution	80 cc.
FeSO <sub>4</sub>	0.01 gm.	H <sub>3</sub> PO <sub>4</sub> , 1.0 N solution	20 cc.
Ca <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub>	2.5 gm.	Distilled water to make	1000 cc.

8. This medium is the same as 1, with the addition of 1 per cent CaCO<sub>3</sub>, weighed out separately, or 0.25 gm. CaCl<sub>2</sub> per liter

## 9. Solid agar medium of Beijerinck

Tap water	1000 cc.	NH <sub>4</sub> Cl	0.1 gm.
Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub>	5.0 gm.	Agar	20.0 gm.
K <sub>2</sub> HPO <sub>4</sub>	0.1 gm.	With or without 2 per cent CaCO <sub>3</sub>	
NaHCO <sub>3</sub>	0.2 gm.		

Medium 10<sup>3</sup>

Media 1, 2, 3, 4, 8, 9 are used for the study of bacteria that are able to oxidize sulfur under neutral or alkaline conditions. Media 5, 6, 7, for the study of bacteria oxidizing sulfur under acid conditions. As a matter of fact, although *Th. thiooxidans* was isolated by means of medium 5, the other media (6 and 7) which were developed later, were found to give much better results. This is due to two factors: *a*, the initial reaction is more favorable for the growth of the organism, *b*, the large amount of buffer (KH<sub>2</sub>PO<sub>4</sub>) does not allow the acid formed from the oxidation of sulfur to change rapidly the reaction of the medium to such a degree of acidity as to injure the further development of the bacteria.

<sup>2</sup> The sulfur and the Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub> are weighed out separately into the individual flasks. Media 5, 6, and 7 are sterilized, on 3 consecutive days in flowing steam, for 30 minutes.

<sup>3</sup> After this paper has been submitted for publication, another solid medium has been developed for the growth of *Th. thiooxidans*, consisting of 1000 cc. distilled water, 5 gm. Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>, 0.1 gm. NH<sub>4</sub>Cl, 0.25 gm. CaCl<sub>2</sub>, 3 gm. KH<sub>2</sub>PO<sub>4</sub> and 20 gm. agar.

As a starting point for the isolation of the microorganisms that are able to oxidize sulfur both under acid and alkaline conditions, two kinds of compost were used, A. The sulfur-floats-soil compost, developed by Lipman, McLean and associates resulted in the isolation of *Th. thiooxidans* described in detail elsewhere (9, 16) both as to methods of isolation, morphological, cultural and biochemical characteristics. B. The alkali-soil-sulfur compost, which consists in composting black alkali soil, having a pH value of 9.6-9.8, with various amounts of sulfur. This compost gave very good results by the use of media 1, 8, 9. At least two organisms have been obtained which are responsible for the oxidation of sulfur under alkaline conditions. These organisms behave in general like *Th. thioparus* and related forms studied by Nathanson (11) Beijerinck (1), Jacobsen (5, 6) and Trautwein (13). But, in addition to some morphological differences, they also show some distinct physiological differences.

Beijerinck reported that *Th. thioparus* when grown on his medium (1), produces a thick pellicle consisting of sulfur enclosing the bacterial bodies. Trautwein reported that his organism (related to *Th. denitrificans*) does not produce any sulfur from the thiosulfate. In our case, an organism was obtained which readily produces sulfur in the presence of  $\text{CaCO}_3$ , but does not produce any in its absence. The idea suggested itself that this may be the explanation of the difference between Beijerinck's and Trautwein's results. Possibly that the  $\text{CO}_2$  produced from the carbonate by the acid formed, interacts with the thiosulfate and gives precipitated sulfur. The cultures from the two liquid media, viz., 1, with the  $\text{CaCO}_3$ , on which sulfur has been precipitated and 2, without the  $\text{CaCO}_3$ , on which no free sulfur was formed, were then transferred upon the solid medium 9, with and without  $\text{CaCO}_3$ . In both cases sulfur was precipitated in the streak when the culture was transferred from flask 1, but no sulfur was precipitated in both cases when culture was transferred from flask 2, indicating that we are probably dealing with two different organisms. The existence of a third organism in the mixture also suggested itself, for reasons stated below. The cultures grown on the liquid were transferred to agar media, back again to liquid media, etc., till the following cultures were obtained:

A. Grew readily on solid and liquid media (1, 8, 9) and precipitated sulfur on these media. On the solid medium, the acid produced from the further oxidation of sulfur, acted upon the  $\text{CaCO}_3$  (when present) producing a clear zone around the streak. This resembles, then, in biochemical characteristics the Beijerinck organism.

B. Grew on solid and liquid media (1, 8, 9) not producing any precipitated sulfur. It produced, however, enough acid to dissolve the  $\text{CaCO}_3$ , when present, and formed a clear zone around the streak on the plate. This would resemble the organism of Trautwein if not for the fact that our culture made the medium always acid, while Trautwein's culture did not produce any acid but when the medium was slightly acid, it actually changed it to alkaline.

C. Grew on the liquid and solid media (1, 8, 9) without producing any sulfur and any acid.

In the case of organisms A and B, the reaction of the liquid medium was changed from pH 9.2 to pH 6.2 and 5.8, respectively, while the sodium thiosulfate all disappeared from the medium in a period of 20 days at 25°C. In the case of organism C, very little of the thiosulfate was oxidized. The peculiar behavior of these three cultures may be due merely to the fact that we had here mixtures of *Th. thiooxidans* and *Th. thioparus* or a related strain.

A comparative study of the oxidation of sulfur by these organisms in the soil, under acid and alkaline conditions, will be made the subject of the following paper.

#### SUMMARY

A comparative review is presented of the various microorganisms concerned in the oxidation of sulfur and of those organisms which are or may become active in the soil.

The classification of sulfur bacteria into "true" and "untrue" or "thiosulfate" (thionic acid) bacteria, as suggested by Omelianski is shown to be untenable. If a physiological basis is to be used for the classification of the sulfur bacteria, they should be grouped as sulfide, thiosulfate, and true sulfur bacteria. Another basis for physiological classification would be that of the optimum reaction for the activity of the organisms. They would then be divided into organisms having their optimum under acid and under alkaline or neutral conditions. However, the division into five groups, based on the physiological and morphological characteristics of the organisms is, for the present, the most suitable classification.

The composition of various media used for the study of bacteria oxidizing sulfur under acid and alkaline conditions is given.

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# THE EFFECT OF LIMES CONTAINING MAGNESIUM AND CALCIUM UPON THE CHEMICAL COMPOSITION OF THE SOIL AND UPON PLANT BEHAVIOR<sup>1</sup>

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## INTRODUCTION

As is shown in the paper of Wheeler and Hartwell (22) and in the résumé of Lipman (10), there are several reasons for the repudiation of the lime and magnesia ratio theory of Loew, as it is generally understood. This hypothesis is constantly recurring because it deals with two substances which are of real interest to agricultural chemists. That calcium and magnesium to some degree and in certain forms and relations are antagonistic has been demonstrated by Loew (12) and others. The idea that they should exist in a special ratio in order that each plant thrive is rather exacting. The researches of Osterhout (16), McCool (15), Gile (3), and True (20) are noteworthy as contributing, in a general way, to this subject. From the work of these men it would seem that the relation between calcium and magnesium as affecting the plant is not a simple one, as supposed by Loew, but an interestingly complex relation which is becoming more thoroughly understood.

The fact that there are large quantities of magnesian limestone in this country makes it important that there should be no unnecessary fears with regard to its use because of the magnesium it contains. It is well known that magnesian and even calcic limes when used in large excess are toxic under certain conditions. On this account it would seem advisable to determine whether magnesian and calcic limes are actually deleterious on different types of soil and in what quantities, in what form, for what plants, and under what conditions. A work so broad as this in short-time experiments can be only approximate and yield hardly more than indications that would be of use to the farmer. Long-time experiments are necessary. The analyses and other data presented in this paper are from plats laid out for experimentation of this nature and, representing the first decade, are necessarily preliminary in some respects.

## HISTORY OF THE EXPERIMENT

The soil, a Miami silt loam, is derived from reworked glacial material laid down as a sediment from quiet water under uniform conditions. It is the

<sup>1</sup> Contribution 281 from the Agricultural Experiment Station of the Rhode Island State College, at Kingston.

<sup>2</sup> The agronomical account of this experiment by Dr. Burt L. Hartwell constitutes Bulletin 186 of the Rhode Island Agricultural Experiment Station.

same as that of the permanent fertilizer experiments which are contiguous. The land was in sod from 1889 to 1892. From that time on until 1909, when this experiment was started, the area was uniformly planted to miscellaneous crops. Throughout these periods no manure or lime was added. In 1909 the plats of  $\frac{1}{8}$  acre were respectively treated with chemicals in the following forms: a high-calcium hydrated lime, a high-magnesium ground limestone, a high-calcium ground limestone, a high-magnesium hydrated lime. One plat serving as check received no lime. Because of difficulties in obtaining the high-magnesium hydrated lime, it was not applied until the next year, 1910. Two additional applications were made in 1914 and 1916, respectively.

The amounts of plant nutrients with which the plats were dressed have been the same each year for all plats and have been deemed ample for the crop planted. Since 1917, every practical opportunity has been taken to include magnesium in the fertilizers and to reduce the proportion of calcium in them. This has led to the use of double superphosphate and low-grade sulfate of potash. The former has a smaller proportion of calcium to phosphoric acid than most forms of commercial phosphate and the latter contains magnesium. No farm manure has been added.

#### A CONSIDERATION OF THE LIME MATERIALS APPLIED

In table 1 are given data concerning the lime materials applied. The mechanical analyses of the 1909 samples are not available. It will be seen that the subdivision of the magnesian limestone is much greater than that of the calcic limestone. The calcic and magnesian hydrates possessed the usual pulverulent character of slaked limes. White (23), and later Hartwell and Damon (6), have done work which indicates that limestones on the soils under consideration by them are roughly proportional in their availability over a season or more to the percentage that will pass through an 80- or 100-mesh sieve. On this basis the magnesian limestone would be more active than the calcic limestone.

The chemical and mechanical analyses correspond closely from year to year of application except for the calcic hydrate in the first year, which contained an abnormal quantity of magnesia. This correlation is to be expected, since in most cases they were obtained from the same source each time and the ground stone and analogous hydrated material are from the same quarry.

The percentage of the limes equivalent to calcium oxide was obtained by titration, with methyl orange as an indicator. These data give an idea as to the relative neutralizing value of the limes and is important inasmuch as the limes have been applied in equal neutralizing equivalents. The relative neutralizing power determined on this basis is given in table 1.

In table 2 is given the amount of the various limes soluble in a liter of water when agitated by bubbling through carbon-dioxide gas for the periods stated. Two-hundred cubic centimeters of distilled water and a 5-gm. sample were

used, titrations being made with methyl orange as the indicator and the results calculated to the basis given. In absolute amounts the agreement is not close with the work of other investigators, who, however, used different conditions, or materials of divergent composition. Relatively they are the same in some cases. MacIntire (14), and also Hammett, in unpublished results of this station, found that the magnesian limestone is less soluble in carbonated water than the calcic limestone, which agrees with data presented. The reason for this is probably that there is a greater tendency on the part of the calcic limestone to form a soluble bicarbonate. However, the alkalinity of a distilled water suspension of magnesian limestone is slightly greater than that of

TABLE I  
*Data concerning the limes applied*

	CALCIC HYDRATE	MAGNESIC LIMESTONE	LCALCIC LIMESTONE	MAGNESIC HYDRATE
1909				
CaO (per cent) .....	61.7	32.4	54.9	45.4
MgO (per cent) .....	10.1	20.8	1 1.0	33.1
Relative neutralizing power .....	133	100	6000	160
Amount added (lbs.) .....	4511	6000	00	3750†
1914				
CaO (per cent) .....	73.4	29.7	50.2	47.4
MgO (per cent) .....	1.0	20.1	2.8	31.7
Relative neutralizing power .....	133	107	100	165
Through 100-mesh (per cent) .....	100.0	85.0	61.0	100.0
Amount added (lbs.) .....	2262*	2820	3000	1819
1916				
CaO (per cent) .....	65.7	26.5	50.4	42.9
MgO (per cent) .....	3.9	20.3	4.2	32.5
Relative neutralizing power .....	145	100	103	168
Through 100-mesh (per cent) .....	100.0	87.0	57.0	100.0
Amount added (lbs.) .....	3096†	4500	4348	2676
pH of distilled water suspension* .....		8.5	8.3	

\* Determined by Dr. P. S. Burgess.

† 50 per cent extra to the south half.

‡ Applied in 1910.

calcic limestone, indicating that the former has a larger number of hydroxyl ions available to neutralize soil acidity under such conditions.

From the results obtained, the conclusion seems warranted that the magnesian limestone, although it is more finely divided than the calcic limestone, becomes available more slowly.

The magnesian hydrate is more soluble in carbonated water than the corresponding calcic hydrate. This would be expected if the magnesium hydroxide is converted into the carbonated form which, unlike the magnesian limestone, is quite soluble. The high alkalinity of these hydrate forms just before

carbonation processes take place would suggest application at a considerable time previous to planting. The solubilities of the hydrates, as shown in table 2, are in the same direction as those obtained by MacIntire, who used the pure oxides.

It can be seen from table 1 that the magnesian limes contain relatively large amounts of calcium. Consequently the system of nomenclature adopted in this paper is purely arbitrary.

TABLE 2  
*Solubility of limes in carbonated water at room temperature*  
Grams equivalent to CaO dissolved in 1 liter

CONTACT	1914 CALCIC LIMESTONE	1916 CALCIC LIMESTONE	1916 MAGNESIC LIMESTONE	1916 CALCIC HYDRATE	1916 MAGNESIC HYDRATE
<i>hours</i>	<i>gm.</i>	<i>gm.</i>	<i>gm.</i>	<i>gm.</i>	<i>gm.</i>
1	0.360	0.326	0.156	0.554	0.705
2	0.378	0.323	0.158	1.256	3.134
4	0.373		0.180		
16		0.383	0.193	0.918	2.229

#### REVIEW OF CROP RESULTS

With the many varieties of crops grown no readily apparent differences have been observed beyond those already noticed in connection with acid- and limed-soil studies. No correlation has been brought out by the crop data accumulated that would show a decided superiority of one form of lime over another. This work tends to corroborate the work of Lipman and Blair (11), who find that magnesian limestones are par with calcic limestones, within the limits of their experiments.

The lack of thrift in a few crops of late years accompanied by such signs as chlorosis has led to the conclusion that the liming has reached the limit of its beneficial effect on certain sensitive plants and has begun to be associated with a slightly toxic action.

The crops grown just before and during the time of the analytical work of this paper, with the yields, are shown in table 3.

TABLE 3  
*Yield per acre of field crops grown during the time of the analytical work, 1919-1921*

	EARLY POTATOES (LARGE) 1919	TIMOTHY, REDTOP, ALSIKE AND MEDIUM RED CLOVER		
		Hay 1920	Rowen 1920	Hay 1921
	<i>bushels</i>	<i>tons</i>	<i>tons</i>	<i>tons</i>
Calcic hydrate.....	152	1.84	0.83	4.43
Magnesian limestone.....	140	1.88	0.75	4.27
Calcic limestone.....	140	1.95	0.68	4.20
Magnesian hydrate.....	162	2.17	0.86	4.24
No lime.....	136	1.39	0.79	3.20

## EXPERIMENTAL METHODS

As previously stated, the plant has failed to show any great differences between the various treatments with soil amendments. Therefore, in order to obtain a more thorough knowledge of conditions, a chemical analysis of the soil was undertaken.

The soil was sampled by means of a soil tube of  $1\frac{3}{4}$ -inch bore and to the depth of 10 inches in one instance and to 12 inches in all other samplings. The borings were evenly distributed over the plat, avoiding the edges. Twenty borings to each  $\frac{1}{8}$  acre plat have been found to represent that area fairly, so this number was taken except in the first set of samples (see table 4). The plats were divided into north and south halves in making borings. Although analytical work was done in some cases on both halves, mostly the determinations from the north halves, which are more uniform, are given in this paper.

The samples of soils from the field were air-dried in subdued light and after they were passed through a 20-mesh sieve the coarse material was discarded.

TABLE 4  
*A synopsis of samples taken*

NUMBER	DATE	DEPTH	BORINGS PER PLAT	REMARKS
		<i>inches</i>		
1*	August 13, 1919	10	12	All plats, ground clear
2	April 26, 1920	12	20	All plats, ground clear
3	August 30, 1920	12	20	Magnesium hydrate, no lime, in stubble
4	November 4, 1920	12	20	All plats, in stubble

\* Taken by C. G. Bridge, formerly assistant chemist at the Rhode Island Agricultural Experiment Station.

A sample in some cases was ground to pass a 100-mesh sieve for such determinations as total nitrogen and loss in weight on ignition. No decided advantages were observed to be gained by this extra subdivision. This is due to the fact that there are probably no inclusions of organic matter by the mineral substances present in the soil, which are not reached by the concentrated acid, and to the fact that, if reasonable care is taken, probably an equally representative sample of the coarser soil can be weighed out.

The methods of the Association of Official Agricultural Chemists (1916) for soils were used in making the ordinary determinations. Special methods will be described with the discussion of data obtained thereby.

The object in view in taking 12-inch samples was to get well below the surface soil, which averages about 7 inches. This method allows for future deepening of the soil by light plowing of the subsoil while keeping well within the limits of possible future sampling of the same surface weight for comparative determinations. Moreover, the roots of many plants extend as far down as this; and, in cases of plants like alfalfa, even beyond. It eliminates the

trouble of dealing with two samples, one of the surface soil, and one of the subsoil. This increase of about 5 inches in depth beyond the surface soil, however, results in a marked dilution of some of the constituents of the surface soil, such as nitrogen and organic matter.

#### MISCELLANEOUS TESTS

In all the samples of soils, the percentage by weight of the soil that would pass through a 20-mesh sieve after air-drying was determined, on an air-dry basis. The figures from this mechanical analysis showed a correlation by half plats in the three different complete sets of samples, indicating that the soil is fairly uniform and that the samples are thus far representative of the half plat. The percentage passing through a 20-mesh sieve averaged about 94 per cent. The fine character of the Miami silt loam becomes apparent at once from these data.

Freezing-point determinations were made on the soils sampled 12 inches deep in April, 1920, from the north halves of the plats. No marked differences were observed between any of the plats under observation. The freezing-point depression, determined from 25 gm. of air-dried soil with 5 cc. of distilled water, is about  $0.081^{\circ}\text{C}$ .

Carbonates were determined in these soils and found to be present in negligible quantity. Only a small amount of carbonates is to be expected, when it is considered that the chemicals were added over 3 years before the taking of the samples.

In the spring of 1920, all the plats were seeded to a mixture of redtop, timothy, and alsike and red clovers. Late in the summer an attempt was made to estimate the relative composition of the flora. Inadvertently the species of clovers and to a lesser extent of the grasses were mixed. From the small amount of data collected, it seemed as if the plants germinated equally well on all plats but that their subsequent development differed. There was a tendency for the redtop to give its best growth on the acid plat, while the timothy did best on the limed areas.

The work was repeated with greater care in the second year of the grasses, namely, 1921. Random samples from about fifteen places, well distributed over the plat, were taken. Each sample had an area of 16 square inches. The plants were dug up by the roots, so that they could be distinguished individually. The timothy was recognized by its basal bulb and the redtop by the absence of the same. The alsike and red clovers were known by the blossom or the characteristic leaf-markings. In case of the timothy and redtop, the number of fruited stalks also was noted.

It seemed from the estimates as if the alsike clover and redtop predominated in numbers and total weight on the acid plat. The alsike clover was about equally developed on all the plats. In competition with timothy and redtop, alsike and red clover thrived about equally well on the limed areas in the



second year of growth. The redtop had more fruited stalks on the acid plat. The reverse was true of the timothy, which had more fruited stalks, greater numbers and a greater total weight, on the limed soils.

All the limed plats were very much alike in general appearance. For this reason, and because they exhibited about the same reaction, only two of the limed plats were sampled.

From the similarity in composition of flora on the limed plats and the marked difference on the acid soil, it would seem that the reaction of the soil is an important factor in a mixed herbage.

TABLE 5  
*Data concerning the plant population*

	REDTOP	ALSIKE CLOVER	TIMOTHY	RED CLOVER
Plants per square yard				
Calcic limestone.....	618 (208)*	192	866 (501)	142
Magnesian hydrate.....	826 (367)	173	1026 (659)	108
No lime.....	982 (466)	319	349 (167)	35
Per cent by numbers				
	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>
Calcic limestone.....	34	10	48	8
Magnesian hydrate.....	39	8	48	5
No lime.....	58	19	21	2
Weight per square yard†				
	<i>gm.</i>	<i>gm.</i>	<i>gm.</i>	<i>gm.</i>
Calcic limestone.....	116	167	643	137
Magnesian hydrate.....	157	167	686	108
No lime.....	203	243	192	41
Per cent by weight				
	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>
Calcic limestone.....	12	16	60	12
Magnesian hydrate.....	14	15	61	10
No lime.....	29	37	28	6

\* Figures in parentheses are numbers of fruited stalks.

† On the basis of oven-dried material.

The yields of hay and rowen are given in table 3 and the data concerning the plant population are tabulated in table 5.

In the late summer of 1920, after the first cutting of the mixed grasses, there was a noticeably better growth of red clover on the acid plat as compared with the limed areas. This was surprising in view of the fact that it is generally believed that red clover thrives best on soils which are nearer the point of neutrality. This phenomenon was repeated in the second growth of 1921. At that time there were more red clover plants on the acid soil than



on the limed areas. The individual plants from the acid soil, on an average, weighed more by about one-half when dried than those on the limed plats. At the first cutting of 1921, the red clover plants from all plats were of about the same weight, but the limed plats surpassed the unlimed area in point of numbers.

#### THE LIME REQUIREMENT AND REACTION OF THE SOIL

Lime-requirement determinations were made in the four sets of samples by the Hopkins method given in the Association of Official Agricultural Chemists Methods for 1916. For comparison the requirement was estimated by the Veitch method, see Hill (7), and the Howard method (8) on the samples taken April, 1920. Results giving the need for lime by the well-known Jones procedure were at hand for the year 1914, and represent the condition of the soil just before the second application of amendments.

The Hopkins-method determinations indicate little difference in requirement among the limed plats, but a marked deviation between limed and unlimed areas. As is well recognized, the need for lime given by this method is low.

A much higher requirement is shown in case of the unlimed plat by the Veitch, Howard and Jones methods, which is more in accordance with the facts as they are known. White (24), using the Veitch method in a comprehensive study, finds the average lime requirement of acid soils in Pennsylvania to be about 3000 pounds of calcium carbonate to the acre, which is lower than the need shown by the acid plat. The limed soils showed a neutral, slightly acid or alkaline test by the Veitch method. The results are listed in table 6. The hydrogen-ion concentration determinations on these soils are compatible with the other estimations of acidity.

The Hopkins-method determinations show that there is a seasonal change in acidity on the limed plats which may be attributed to the crop or to the leaching by the heavy midsummer rainfall. The requirements after the crop of potatoes were quite high compared with those determined the following spring. The depths of the samples taken after potatoes differ from subsequent ones by 2 inches of subsoil, but it would hardly seem that this would give rise to the differences obtained. This acidity must be fixed in the air-dry soil because the determinations were made simultaneously, after the taking of the samples. This observation, namely, seasonal fluctuation in reaction of the soil, was corroborated by determinations made on soils sampled August, 1920, where the magnesian-hydrate plat shows a summer increase in acidity. Howard (9) finds a similar variation in the need for lime by soil of this type.

In estimating 0.05*N* acetic acid solubles, the amount of acetic acid absorbed or neutralized by the soil was noted. Twenty cubic centimeters of the acid were titrated before and after extraction of the soil, and the difference between these two figures in cubic centimeters of alkali (approximately 0.08 *N*) is given in table 6. The relative reaction is exhibited and correlates with the determinations of lime requirement.

There are no large differences in acidity which can be assigned to the different kinds of lime. Evidently there is about the same amount of active base in these plats and any differences must be correlated with other factors than the final reaction. This is essentially the experience of Lipman and Blair (11), who, however, worked chiefly with the calcic and magnesian limestones.

#### ALUMINUM EXTRACTABLE BY SOLVENTS

Many acid soils give up soluble aluminum when treated with potassium-nitrate solution. With this in mind, the soils under examination were extracted with normal potassium-nitrate solution and other solvents to see whether there was any difference in soluble aluminum. The potassium-nitrate extract was obtained from the regular determinations of lime requirement by the Hopkins method. With normal ammonium-chloride solution the same procedure was followed as that used in connection with potassium nitrate.

In treating the soils with carbon dioxide, 50 gm. was used with 250 cc. of distilled water in a Kjeldahl flask and the system maintained saturated under a slight pressure (the acid-column of the Kipp generator) for about 5 days with intermittent shaking and agitation by driving carbondioxide gas through the muddy suspension. The five soils were supplied with carbon-dioxide gas from the same generator. This is essentially the method proposed by Hartwell (4).

Trials were made with acetic acid of varying strength to ascertain a concentration which would be sensitive to differences in soluble aluminum in the soil. Twentieth-normal approached nearest to the requirements. The manipulation used in connection with this acid was as follows: 50 gm. of soil were shaken in an end-over-end shaking machine for 3 hours with 150 cc. of approximately 0.05*N* acetic acid.

Filtrations, in all cases, were made through filter paper and this process was repeated until a clear filtrate was secured. The silica in solution was found to be negligible in most instances. The aluminum and iron were precipitated with dilute ammonia water. The iron present was determined by titration against permanganate, and subtracted from the weight of ignited oxides, in case of the acetic-acid extractions; but this correction was not applied with the other methods of procedure, because the ashed precipitate seemed to be free from iron as indicated by color. At the most the iron extracted was only a small fraction of the aluminum oxide obtained. Tests were made for phosphoric acid with the use of ammonium molybdate, but there was none present.

The data enumerated in table 7 will be discussed bearing in mind the solvents and methods used.

No weighable aluminum oxide was obtained from the limed soils with normal potassium-nitrate and normal ammonium-chloride solutions, nor with saturated carbon-dioxide water. A fair amount was secured from the acid plat

TABLE 6  
*Lime requirements and reaction of soil in north halves of plats*  
 Requirements in pounds of CaO per acre-foot of 3,000,000 pounds air-dry soil

LIME REQUIREMENT METHODS	CALCIC HYDRATE	MAGNESIC LIMESTONE	CALCIC LIMESTONE	MAGNESIC HYDRATE	NO LIME	DATE SAMPLED	DEPTH TAKEN
	lbs.	lbs.	lbs.	lbs.	lbs.		inches
Jones*	3080	3290	2970	3190	5080	1914	12
Hopkins	80	95	153	105	630	Aug., 1919	10
Hopkins	22	45	35	34	512	Apr., 1920	12
Hopkins				97	473	Aug., 1920	12
Hopkins	21	33	29	22	517	Nov., 1920	12
Howard	3300	3600	3900	3600	5400	Apr., 1920	12
Veitch	Alkaline	Slightly alkaline	Slightly acid	Alkaline	3900	Apr., 1920	12
	pH†	pH†	pH†	pH†	pH†		
	7.2	7.2	6.6	7.4	5.2	Nov., 1920	12
	6.6	6.3	6.4	7.1	4.9	May 12, 1920	7†
	6.3	6.1	6.2	6.4	4.7	July 5, 1920	7†
	6.3	6.1	6.3	6.6	4.9	Aug. 16, 1921	7†
Relative 0.05 N acetic acid absorption	3.9	4.4	3.9	4.2	1.5	Aug., 1919	10

\* Determined by G. E. Merkle.

† Determined by Dr. P. S. Burgess.

‡ Determined on moist soil.

with these solvents. Where 0.05*N* acetic acid was employed a small quantity was brought into solution from the limed plats and a much larger amount from the unlimed soil. There seems to be little variation in the active aluminum attributable to the different types of lime, as revealed by the acetic-acid digestion.

This work differs from that of Spurway (19) who concludes from leaching experiments with distilled water that calcium carbonate tends to bring the aluminum into solution. Perhaps it might be said that applications of calcium carbonate had resulted in leaching out all the soluble aluminum present in the soil. The acetic-acid treatment, as carried out in this work of the writer, indicates that there is readily soluble aluminum at hand but it is evidently held in an insoluble form by the alkalinity of the soil and is brought into solution by the soil acidity.

TABLE 7  
*Aluminum oxide extracted by solvents from soil in north halves*  
Parts per million of air-dry soil

SOLVENT	CALCIC HY- DRATE	MAG- NESIC LIME- STONE	CALCIC LIME- STONE	MAG- NESIC HY- DRATE	NO LIME	DATE SAMPLED	DEPTH TAKEN
	<i>p.p.m.</i>	<i>p.p.m.</i>	<i>p.p.m.</i>	<i>p.p.m.</i>	<i>p.p.m.</i>		<i>inches</i>
Normal potassium nitrate....	None	None	None	None	91	August, 1919	10
Normal potassium nitrate....	None	None	None	None	82	April, 1920	12
Normal potassium nitrate....	None	None	None	None	82	August, 1920	12
Normal potassium nitrate....	None	None	None	None	92	November, 1920	12
Normal ammonium chloride..	Trace	Trace	Trace	Trace	79	April, 1920	12
0.05 <i>N</i> acetic acid.....	120	110	150	100	440	August, 1919	10
Carbonated water.....	None	None	None	None	47	April, 1920	12

The evidence put forth shows that with these soils active aluminum is an indicator of sourness. Previous work has demonstrated (5) that aluminum is toxic to certain plants and therefore it is probable that it is one of the causes of the inability of the acid soils of this type to produce satisfactory yields of some crops.

#### THE CALCIUM AND MAGNESIUM IN THE SOIL

Efforts to ascertain what strength of solvent would bring out these elements in a ratio that might be correlated in some way with the crop response have been more or less futile. In this paper the work of Loew and his associates on this problem has received most attention (12).

Five solvents were used in the present study, as follows: (a), normal ammonium-chloride solution; (b), the saturated carbon-dioxide water, other details of which are given under the heading, "Aluminum oxide extractable by solvents;" (c), the normal potassium-nitrate solution of the Hopkins method; (d), the 10 per cent hydrochloric acid recommended by Loew (12); (e), the hot, strong hydrochloric acid, as used in the Hilgard method. The calcium and

magnesium were determined gravimetrically by well recognized methods of procedure. The results of this work are given in table 8.

In the carbon-dioxide water determinations a larger proportion of CaO than MgO was brought into solution. In the digestion where hot, strong acid was used nearly the reverse is true. This finding would indicate that the magnesium is present in a more difficultly soluble form than the calcium. Apparently there is an abundance of available calcium and magnesium for plant-food even on the sour soil, as shown by solubility in carbonated water. The attack of the cold 10 per cent acid recommended by Loew is about half

TABLE 8

*Amounts of CaO and MgO extracted by solvents from the soil in the north halves from 12-inch samples taken April 26, 1920*

Parts per million of air-dry soil

	CALCIC HYDRATE	MAGNESIC LIMESTONE	CALCIC LIMESTONE	MAGNESIC HYDRATE	NO LIME
Carbonated water:					
CaO (p.p.m.).....	478	357	503	368	172
MgO (p.p.m.).....	64	207	77	212	80
Ratio CaO-MgO.....	7.5-1	1.7-1	6.5-1	1.7-1	2.2-1
Normal ammonium chloride:					
CaO (p.p.m.).....	1207	743	.....	796	209
MgO (p.p.m.).....	71	262	57	281	31
Ratio, CaO-MgO.....	17.0-1	2.8-1	.....	2.8-1	6.7-1
Normal potassium nitrate*					
CaO (p.p.m.).....	1280	860	1210	780	280
Loew's 10 per cent cold HCl:					
CaO (p.p.m.).....	.....	1350	1730	1420	400
MgO (p.p.m.).....	860	1170	1010	1400	780
Ratio, CaO-MgO.....	.....	1.2-1	1.7-1	1.0-1	0.51-1
Hilgard's 25 per cent hot HCl:					
CaO (p.p.m.).....	4100	2820	3600	3750	2810
MgO (p.p.m.).....	3450	3720	3200	4170	3250
Ratio, CaO-MgO.....	1.2-1	0.76-1	1.1-1	0.90-1	0.87-1

\*10-inch sample taken August, 1919.

as vigorous as that of the hot concentrated acid, and in addition a slightly higher proportion of CaO to MgO is removed from the soil.

It is noticeable that the normal potassium-nitrate and normal ammonium-chloride solutions approach the 10 per cent hydrochloric acid (about 3*N*) in their power to extract calcium. This would indicate that there is considerable change of bases, presumably a replacement of the calcium in the zeolitic minerals by potassium and ammonium ions. With the ammonium-chloride reagent the highest proportion of calcium to magnesium is obtained. This is contrary to ideas of some who think that the ammonium chloride might exert a selective action on the magnesium. The amount of magnesium dissolved is about the same as that obtained by the carbon-dioxide treatment,

except on the acid plat, where it is much less, which would make one suspect that the ammonium chloride might be more sensitive to differences in magnesia availability. The presence of a smaller amount on the unlimed plat is in accordance with the work of Lyon (13) who finds that additions of calcium tend to make the magnesium more soluble, as shown by the leachings, and also agrees with the availability as estimated by the soybean (table 9).

The acid plat compares closely in the ratio of soluble MgO to CaO with the soils receiving applications of magnesian limes. The conclusion seems justified that the magnesian limes represent more closely the combination of MgO and CaO which was present in the soil originally, and that the magnesian hydrate is converted into a form similar to that in which the magnesian limestone exists in the soil after application.

#### THE PLANT AS A LIME-AND-MAGNESIA ANALYST.

Up to this time, several crops had been sampled and analyzed for calcium and magnesium and the ratios of absorption calculated. The data are given in table 9. The yields of plants do not show any marked variation with changes in the ratio of CaO to MgO in the analyses of the dried substance.

It appears that the legumes absorbed a higher ratio of calcium to magnesium than the endive, except on the soils given magnesian limes, where the ratios are about the same.

On the unlimed soil and the plats given calcic limes the percentage of calcium oxide in the plant is usually high compared with the soils treated with magnesian limes. On the other hand, the amount of magnesium oxide absorbed by the plants is highest on the soils receiving magnesian limes. From the fact that the yields are fairly uniform on all plats, it appears that the plants analyzed are able to accommodate themselves without injury within certain limits, to changes in the soil solution. Moreover, luxury consumption of an element when present in excess is not uncommon in the plant kingdom.

Parker and Truog (17) come to the conclusion that there is a close relation between the nitrogen and calcium in plants but not between their contained magnesium and nitrogen. This relation is evident with the majority of plant analyses they considered. The analyses of the plants of this project do not corroborate this theory, where in case of the acid plat the percentage of calcium in the plants is about the same as for the lime-treated soils, but the percentage of nitrogen and magnesium is low in comparison with the limed areas. In the soybean, changes in the absorption of calcium are not paralleled by similar fluctuations in the percentage of nitrogen.

The solvent (referring to tables 7 and 8) that comes nearest to extracting from the soil magnesium and calcium oxides in the ratio in which they are contained by the plants analyzed is the saturated carbon-dioxide water. This solvent would be more appropriate than those more vigorous in their action which are used by Loew and his associates.



TABLE 9\*

*Calcium and magnesium oxides in plant parts*

	CALCIC HYDRATE	MAGNESIC LIMESTONE	CALCIC LIMESTONE	MAGNESIC HYDRATE	NO LIME
Soybean hay, 1913; Whole plat; Analyses on air-dry sample					
Acre yield of hay (tons).....	3.76	3.82	3.94	4.06	2.66
CaO (per cent).....	1.55	1.40	1.94	1.39	1.58
MgO (per cent).....	0.50	0.73	0.37	0.86	0.27
Ratio, CaO-MgO.....	3.1-1	1.9-1	5.2-1	1.6-1	5.8-1
Nitrogen (per cent).....	2.84	3.02	2.98	3.04	2.42
Soybeans for silage, 1914; North halves; Analyses on moisture-free hay; Acre yields are for whole plat					
Acre yield of silage (tons).....	7.82	6.86	8.10	10.52	9.34
CaO (per cent).....	1.89	2.10	2.52	1.59	2.39
MgO (per cent).....	0.60	1.04	0.46	1.21	0.28
Ratio, CaO-MgO.....	3.2-1	2.0-1	5.5-1	1.3-1	8.5-1
Nitrogen (per cent).....	3.49	3.67	3.68	2.96	2.29
Removed per acre:					
CaO (pounds).....	96	83	110	69	101
MgO (pounds).....	30	41	20	52	12
Nitrogen (pounds).....	176	145	161	128	96
Endive, aerial portion, 1917; North half; Analyses on dried sample					
Acre yield, green (tons).....	18.62	21.26	24.00	23.81	19.54
CaO (per cent).....	1.42	1.25	1.57	1.29	1.48
MgO (per cent).....	0.65	0.86	0.52	1.14	0.52
Ratio CaO-MgO.....	2.2-1	1.5-1	3.0-1	1.1-1	2.8-1
Nitrogen (per cent).....	2.41	2.23	2.08	2.35	1.88
Removed (per acre)					
CaO (pounds).....	32	33	48	37	38
MgO (pounds).....	15	23	16	33	13
Nitrogen (pounds).....	55	58	64	68	49
Winter beans, 1917; South half; Analyses on moisture-free leaves					
Acre yield of beans (bushels).....	15	19	18	19	19
CaO (per cent).....	4.89	.....	.....	4.27	3.45
MgO (per cent).....	0.98	.....	.....	2.14	0.80
Ratio, CaO-MgO.....	5.0-1	.....	.....	2.0-1	4.3-1

\* The majority of the analyses in table 9 were made by G. E. Merkle, formerly assistant chemist at the Rhode Island station.

## DETERMINATIONS RELATIVE TO NITROGEN AND ORGANIC MATTER.

Most soils are heterogeneous in their nature. Waynick (21) and others have amply demonstrated this by statistical methods. Consequently a person in making determinations on soils, particularly of nitrogen, should not only realize but estimate his probable error, both of sampling in the field and



of analytical work in the laboratory. In this paper percentages are given to the thousandths place and this is further limited by the probable error. The formulas used are taken from Wood and Stratton (25)—probable error of any of a series of results,  $P. E. = \pm .67 \sqrt{\frac{\sum d^2}{n-1}}$ ; probable error of average of a series of determinations,  $P. E. = \pm .67 \sqrt{\frac{\sum d^2}{n(n-1)}}$ .

The figures showing the determinations of nitrogen and organic matter are arranged in table 10.

The first set of samples was taken in August, 1919, to the depth of 10 inches, after a crop of early potatoes. Estimations of total nitrogen were made by the Kjeldahl method for soils without modifications (1). The plats limed with calcic and magnesian hydrates have about the same percentage of nitrogen when the probable error is taken into account. The sour soil ranks with the hydrates. The ground magnesian limestone and the corresponding calcic limestone have a slightly higher percentage, with any superiority in favor of the former. The probable error of sampling these soils was not determined, but subsequent work will show that with samples taken 2 inches deeper it is not very great.

The second samples were taken to the depth of 12 inches in April, 1920, after a fall seeding of wheat which was winter-killed, and after the spring fertilizer (containing 20 pounds of nitrogen per acre) was applied. The 2-inch increase has a marked diluting effect and the differences readily visible before are less prominent. There remains an indication that the magnesian limestone is superior in the percentage of total nitrogen, while the other treatments may be considered about alike.

The last samples were obtained in the fall of 1920 after a crop of mixed grasses and were taken to the depth of 12 inches. On looking at table 10, it will be seen that there is a slight difference credited to the magnesian limestone while the other soil treatments leave the soils alike. The slightly lower percentage of all analyses compared with those on soils taken in April may be partly explained by the compactness of the soil. The average weight of 10 borings of the April samples to the same depth, dry soil, was 12.45 pounds as compared with 13.00 pounds for those taken in November. The November samples contained a slightly greater weight per boring and consequently more subsoil than the April samples. This dilution of the surface soil would slightly reduce the percentage of nitrogen. In addition, it may be partly attributed to the taking of the November samples in the grass stubble. If considerable nitrogen is held in the root system, the reduction of the nitrogen percentage in the soil due to greater compactness would be accentuated.

TABLE 10  
*Determinations relative to nitrogen and organic matter from the north halves on a moisture-free basis*

	CALCIC HYDRATE	MAGNESIC LIMESTONE	CALCIC LIMESTONE	MAGNESIC HYDRATE	NO LIME	DATE SAMPLED	DEPTH TAKEN
	per cent	per cent	per cent	per cent	per cent		inches
Loss-on ignition.....	5.9	6.8	6.1	5.5	5.8	Aug., 1919	10
Loss-on-ignition.....	5.4	5.7	5.8	5.3	5.7	Apr., 1920	12
Humus, Rather method.....	2.56	2.77	2.73	2.43	2.38	Apr., 1920	12
Humus, A.O.A.C. method.....				2.36	2.42		
Total nitrogen.....	0.150 $\pm$ 0.002	0.188 $\pm$ 0.005	0.164 $\pm$ 0.002	0.148 $\pm$ 0.003	0.144 $\pm$ 0.002	Aug., 1919	10
Total nitrogen.....	0.132 $\pm$ 0.004	0.146 $\pm$ 0.001	0.139 $\pm$ 0.004	0.127 $\pm$ 0.004	0.137 $\pm$ 0.004	Apr., 1920	12
Total nitrogen.....				0.123 $\pm$ 0.004	0.129 $\pm$ 0.004	Aug., 1920	12
Total nitrogen.....	0.128 $\pm$ 0.002	0.132 $\pm$ 0.002	0.122 $\pm$ 0.002	0.121 $\pm$ 0.004	0.124 $\pm$ 0.004	Nov., 1920	12

At the time of taking the April samples, duplicates were secured from both the north and the south halves of the magnesian limestone plot. A series of about 12 nitrogen determinations was made on each of these 4 samples. The percentages of nitrogen on a moisture-free basis with the probable error of the average are as follows: north half,  $0.146 \pm 0.002$ ;  $0.149 \pm 0.002$ ; south half,  $0.129 \pm 0.002$ ;  $0.137 \pm 0.002$ .

Humus determinations were made by the Rather method (18), which was found to be more accurate, and to consume less time, than the usual procedure where the soil is extracted with ammonia. The estimations of humus and loss on ignition show a slight superiority in content of organic matter in favor of the ground limestones as compared with the hydrates. The loss on ignition figures are accurate to tenths of one per cent.

From a study of the soil nitrogen and organic matter nothing very extraordinary has been observed. It is a little too early, as yet, to state definitely that the magnesian limestone surpasses the other forms in nitrogen accumulation to any economic extent. No decided superiority of the calcic limes is apparent from the analyses under discussion. The findings here also agree with those of Ellett (2), who perceives no difference in the percentage of soil nitrogen outside his limit of error, over a series of years, between an unlimed soil and a soil treated with burnt lime.

#### SUMMARY AND CONCLUSIONS

1. In 11 years, 3 applications of hydrated magnesian and calcic limes and ground magnesian and calcic limestones, in carefully controlled field experiments, show little difference in crop yields due to the various forms.
2. Hydrated limes and limestones, high in either calcium or magnesium, act about alike as neutralizers of soil acidity when applied in equivalent amounts, as determined by titration.
3. Calcic and magnesian limes have rendered the aluminum of the soil relatively insoluble. Active aluminum was present on the acid plot.
4. Applications of magnesian limes tend to maintain in these soils a ratio of calcium to magnesium similar to that of the unlimed soil.
5. Plants were not influenced by the varying ratios of CaO to MgO, found in this experiment, but were sensitive to soil reaction.
6. Magnesian limestone shows a slight tendency to increase the percentage of total nitrogen in these soils.
7. Hydrated calcic and magnesian limes up to the present time have not caused any reduction in the percentage of nitrogen, but have resulted in a slight decrease in the percentage of organic matter in the soil.

The author is indebted to Dr. Burt L. Hartwell for direction in conducting the problem and to Mr. P. H. Wessels and Dr. P. S. Burgess of the Rhode Island Agricultural Experiment Station for advice and suggestions.

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# THE COMPARATIVE AGRICULTURAL VALUE OF INSOLUBLE MINERAL PHOSPHATES OF ALUMINUM, IRON, AND CALCIUM<sup>1</sup>

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## INTRODUCTION

"Phosphorus is the only element that must be purchased and returned to the most common soils of the United States. Phosphorus is the key to permanent agriculture on these lands." This statement of C. G. Hopkins (29) emphasizes the extreme importance of the phosphorus problem in modern agriculture; especially at the present time when the seriousness of the world food situation is making an urgent appeal to agriculturists to increase and to maintain permanently the fertility of all tillable soils.

The acute shortage of transportation facilities has placed farmers, not conveniently situated near phosphate-producing centres, at a disadvantage with regard to procuring phosphorus at other than exorbitant prices. This has resulted in a world-wide prospecting for phosphate deposits and has caused considerable speculation as to the feasibility of utilizing iron and aluminum phosphates for agricultural purposes.

In spite of the fact that a considerable amount of work had been done that demonstrates the value of aluminum and iron phosphates, the general belief is that they have little significance from an agricultural point of view. The fact that they are practically useless for acid phosphate manufacture, combined with their low solubility in citric acid and ammonium citrate solutions is probably the main cause for the popular conception of their agricultural value.

There are also numerous statements by eminent scientists scattered throughout the literature in which aluminum and iron phosphates are referred to as being particularly unavailable as plant-food. The fleeting action of super-

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phosphates on soils rich in aluminum and iron oxides, for example, is ascribed to the conversion of this phosphate into aluminum and iron phosphates.

It was the object of the experiments reported in this paper to determine the comparative values of various phosphates of aluminum, iron and calcium which occur in nature, and simultaneously to determine how they are affected by diverse collateral treatments.

#### REVIEW OF LITERATURE

##### *Some fundamental considerations*

A fundamental fact, which has a very important bearing on the phosphate problem in soils was brought to light by the work of Schloesing and Kossovitsch. In 1899, Schloesing (67) demonstrated the fact that plants can obtain their phosphorus from very dilute solutions, solutions containing only 1 to 2 mgm. phosphoric anhydride per liter. This emphasizes the importance of naturally dissolved phosphates in the soil solution for plant nutrition. Kossovitsch (37) repeated these experiments, verified Schloesing's results and showed simultaneously that the relative feeding powers of plants do not rest solely on their ability to utilize the phosphorus occurring in dilute solutions. Flax, when compared with mustard and peas, has but feeble powers to utilize the phosphorus of tricalcium phosphate rock, but was shown to make good growth on a nutrient solution, which contained only 1.3 mgm. of phosphoric anhydride per liter.

From the work of Schloesing one might at first conclude that the plant roots exert a solvent action on phosphates. Sachs (65) in 1860, demonstrated that plants roots were capable of corroding marble plates. In 1896, Czapek (13) conducted extensive investigations to determine whether roots excrete or secrete acids, which might function in dissolving plant-food. Eventually he concluded that carbonic acid was the only acid given off in considerable quantity by live roots of plants. In 1902, Kossovitsch (37) demonstrated clearly that the plant roots themselves and not the nutrient solution were responsible for obtaining phosphorus from phosphorite. The following device was employed by him to determine this factor: Plants were grown in two sets of cylinders. In the one set, sand mixed with tricalcium phosphate was used as a medium for the plants to grow in. Five liters of nutrient solution were passed daily through each cylinder. In the second set, pure sand was used as a medium for growth. As in the above case, five liters of nutrient solution were added daily with the exception that the nutrient solution was first made to pass through another cylinder containing a mixture of quartz sand and tricalcium phosphate and in which no plants were growing. If the nutrient solution acted as a solvent of the phosphate, the plants in the second set of cylinders should have made a fair growth. The plants grew well in the first set and made hardly any growth in the second, proving that if the nutrient solution exerted any solvent action on the tricalcium phosphate, its action was very slight and that the action of the roots themselves was a very much more important factor. In 1911, Prianishnikov (61) made the claim that iron and aluminum phosphates were gradually decomposed by water and that root excretions do not play the important rôle in assimilation of these phosphates that has usually been ascribed to them.

##### *Varying ability of plants to assimilate phosphorus from insoluble phosphates*

In 1893, Balentine (3) working at the Maine Agricultural Experiment Station reported that *Graminae* were benefited more by acid phosphate than by redondite and rock phosphate, and that plants of the *Cruciferae* family were especially strong feeders on rock phosphate. Two years later, Merrill and Jordan (42) placed the four botanical families studied in the order given below as regards their foraging powers for insoluble phosphates.



1. *Leguminosae* as represented by peas and clover.
2. *Cruciferae* as represented by turnips and ruta-bagas.
3. *Graminae* as represented by barley and corn.
4. *Solanaceae* as represented by tomatoes and potatoes.

The insoluble phosphates employed in this investigation were Florida rock phosphate, iron phosphate, and aluminum phosphate.

Kossovitsch at various times between 1898 and 1910 made mention in his writings concerning the feeding powers of different species of plants. In 1901 (36), he commented on the strong feeding powers of buckwheat and mustard when grown with phosphorite as a source of phosphorus. In a later publication (39) in which he summarized his work on the utilization of phosphorite by mustard, clover, oats, and flax, he placed these plants in the order in which they are here mentioned as regards their powers to utilize phosphorite. It should be observed that this order is somewhat similar to that put forth by Merrill and Jordan. Kossovitsch (38) also tried to correlate the feeding powers of plants with their ability to excrete carbonic acid, but the difference in the amounts excreted did not justify the drawing of any definite conclusions.

Schreiber (68) experimented with eleven species of the *Graminae*, nine of the *Leguminosae*, three of the *Cruciferae*, and eleven miscellaneous plants. The *Leguminosae*, the *Cruciferae*, and buckwheat utilized mineral phosphates to a considerable extent, whereas the *Graminae*, flax, tobacco, carrots, asparagus, beets, and potatoes showed little solvent powers.

Wheeler and Adams of Rhode Island (82, 83), Prianishnikov (56, 57), Bonomi (5), Gedroits (23), Chirikov (Tschirikov) (11), Semushkin (69), and Söderbaum (72), are among other workers who have drawn attention to the individuality of plants with respect to the topic under discussion. In nearly all these cases, their results agree in a general way with those of Merrill and Jordan. The work of the above investigators will be considered later in connection with another phase of our problem.

Emil Truog (76, 77) has propounded a theory to explain the individuality of plants with regard to their feeding powers. Plants with a high calcium content he stated, have a relatively high feeding power for the phosphorus in phosphorites. For plants with relatively low calcium content, the reverse is true. Clover, alfalfa, peas, buckwheat, and several of the *Cruciferae* have high calcium content and are, therefore, according to this theory, powerful feeders on insoluble phosphates. Corn, rye, oats, wheat, and millet fall in the opposite class. A calcium oxide content of less than 1 per cent may be considered low. In another publication (78), Truog claimed that high internal acidity of roots is accompanied by high feeding powers for calcium. Logically then, plants with roots of high internal acidity are capable of utilizing insoluble phosphates with greater success than plants with roots of relatively lower internal acidity. It is clear that the individuality of the plants is a large factor when the availability of phosphates is being considered.

#### *Effect of soil on availability of insoluble phosphates*

In studying this question three characteristics of soil have been considered by workers:

1. Mechanical composition.
2. Amount of organic matter in soil.
3. Reaction of the soil.

It is generally held (41) that it is preferable to use bone meal and basic slag on warm sandy soils. Soluble phosphates are put to better use on heavier clay soils. Wheeler and Adams (83) claimed that the addition of three-fourths to one ton of limestone per acre removes the drawback of using soluble phosphates on light sandy soils. On peat and muck soils, the first applications of soluble phosphates are ineffective, due to their entering into colloidal combinations, but after these demands have been met, their effects are noticeable. Concerning the reaction, predominant opinion asserts that soluble phosphates are employed with the greatest success on calcareous soils (14, 27, 49). Hilgard (27) in his celebrated work,



"Soils," made the following statement, ". . . in the presence of high lime percentages, relatively low percentages of phosphoric acid and potash may nevertheless prove adequate; while the same or even higher amounts, in the absence of satisfactory lime percentages, prove insufficient for good production." Paturel (49), Deherain (14) and others claimed that unless sufficient lime be present, the phosphoric acid is fixed by aluminum and iron oxides into unavailable combinations. On the other hand, this view appears contradictory to the observations of Schloesing, fils, regarding the solubility of phosphoric acid in the presence of carbonate of lime (66), but natural conditions seem fully to justify Hilgard's conclusions. Numerous investigators found aluminum phosphates to be very beneficial to plant growth provided they were employed on soils well supplied with lime. Results in Maryland (50), France (1), and Rhode Island (82, 83) all show that favorable results with aluminum phosphate have always been obtained when the phosphate is used in connection with lime or on soils naturally calcareous. When tricalcium phosphate is employed, the best immediate results seem to be obtained on soils not saturated with bases (24) or on soils well supplied with organic matter (28, 82).

*Effect of nitrogen compounds on availability of insoluble phosphates*

Prianishnikov and a large number of other Russian workers have studied very carefully the effect of various nitrogen compounds on the availability of insoluble phosphates. All the results agree in general that ammonium sulfate enhances the availability of insoluble phosphates and that ammonium nitrate likewise increases the availability, but to a lesser extent. Sodium nitrate either has no effect or depresses the availability. Calcium nitrate is similar in its effect to sodium nitrate, but less marked. These results are due to inherent properties of the salts themselves and not to their conversion into other compounds, for example the formation of nitric acid as the result of nitrification of ammonium salts. Kossowitsch (36) was responsible for the classic work in regard to the effect of ammonium salts. In experiments in which the possibility of nitrification being a factor was carefully prevented, he confirmed in all instances the deductions of Prianishnikov. Wheeler and Adams (83) commenting upon Warrington's work (81) seem to be of the opinion that with aluminum phosphates results would have been established which would be the reverse of those given above. The fact that nitrification materially affects the availability of insoluble phosphates has been definitely established by the investigations of Hopkins and Whiting (30). Söderbaum (72) checked up Prianishnikov's deductions. He believed that the physiological reaction of the accompanying nitrogenous fertilizer plays an important part, but claimed that other factors, such as kind of plant, soil and other collateral treatments used, may lessen or even reverse the influence of this factor. This point is well brought out by Chirikov (10) who found that when calcium nitrate replaced ammonium sulfate in his buckwheat cultures, the yields were not reduced, but increased. Nedokuchaev (46) working with different crops, oats and flax, reported that yields were lower where calcium nitrate was used in lieu of ammonium sulfate. On the whole Prianishnikov's deductions seem to be accurate, but we should bear in mind that no hard and fast rule can be laid down. In work on the availability of phosphates, the accompanying nitrogenous fertilizer is a factor that must be remembered, especially when we attempt to make generalizations from our results.

*Effect of lime on availability of insoluble phosphates*

When the effect on the availability of insoluble phosphates was considered, the influence of lime came up for discussion since the reaction of the soil and lime content of the soil are closely interrelated. Some further opinions on the effect of lime follows. Prianishnikov (61) divided the phosphates into two groups; the one, including tricalcium phosphate, bone meal, and phosphorite, consists of those of which the assimilation is markedly reduced by the lime; the other, including acid phosphate (mono- and di-calcium phosphates), Thomas slag,

mono-potassium phosphate, iron phosphate, and aluminum phosphate, consists of those unaffected by the addition of lime or even benefited by it. The studies were made in sand cultures. The crops employed were barley, peas, oats, wheat, and buckwheat. In all cases, however, where ammonium nitrogen was substituted for nitrate nitrogen, liming was beneficial. Shulov (71) in studies similar to those of Prianishnikov, determined that the assimilability of pure ferrous phosphate and vivianite was unaffected by lime; that of tricalcium phosphate, in the forms of bone meal and phosphorite, was adversely affected; and that of superphosphate, precipitated phosphate and Thomas slag was only slightly reduced. Gaither (21) explained the lack of harmful effects of lime upon the availability of soil phosphates as due to its action in replacing iron and aluminum in combination with phosphorus and so rendering the phosphates more soluble. Gaither used 0.2 *N* nitric acid as a solvent for determining available phosphorus. Wheeler and Adams (84) pointed out that, in the phosphate experiments at Rhode Island, iron and aluminum phosphates were more efficient than floats on limed land. This agrees with the findings of Prianishnikov.

*Effect of various solvents on the availability of insoluble phosphates*

It is beyond the scope of this work to enter into the controversy as to which solvents of phosphates can be used for determining their availability to plants. Some literature which has a bearing on this work is quoted. Risler (64) claimed that carbonic acid has much less solvent action on aluminum and iron phosphates than on calcium phosphates. Wagner (80) and later Storer (73) claimed that alkalies, such as sodium carbonate, ammonium carbonate, etc., can dissolve phosphates of iron and aluminum. Cameron and Bell (9) claimed to have proved that soil phosphates are decomposed or hydrolyzed by water with formation of other phosphates containing relatively more of the base. Zecchini (85) reported that aluminum and iron phosphates are very insoluble except in alkaline solution. Gedroits (22) worked on solubility of phosphates in 2 per cent acetic and citric acids. The relative solubilities in acetic acid were tricalcium phosphate, aluminum phosphate, ferric phosphate, in the order named; in citric acid dicalcium phosphate and aluminum phosphate were equally soluble, ferric phosphate less soluble. In growing plants in sand culture with these phosphates, the aluminum phosphate pots gave the highest yield, tricalcium phosphate was second, and iron phosphate pots a close third. Truog (75) questions the whole idea of employing chemical solvents as a means for determining the availability of different phosphates, basing his deductions on favorable results obtained with phosphates of aluminum and iron, which are, as a general rule, less soluble than calcium phosphate in such solvents. Elliot and Hill (16) had before this arrived at the same conclusions. Fraps (19), on the other hand, proposed 0.2 *N* nitric acid as the solvent to indicate the available supply of phosphorus in the soil. He asserted that in pot experiments, the phosphoric acid removed by the crops is closely related to the quantity of "active" phosphoric acid. "Active" phosphoric acid is defined as that amount which dissolves in 0.2 *N* nitric acid.

Several workers have indicated the value of dehydrating aluminum phosphate to render it more valuable as a fertilizer. The investigators at the Rhode Island Agricultural Experiment Station have always included roasted redondite in their comparative phosphate tests and have drawn attention to the value of dehydration. Morse (44) found that roasting increased the solubility of aluminum phosphate in neutral ammonium citrate, but pot and field tests failed to verify the laboratory indications of availability. Pilon et al (54) described a method for roasting double phosphates of iron and aluminum in order to render the combined phosphoric acid soluble in ammonium citrate. Fraps (20) pointed out that ignition increases the solubility of wavellite, dufrénite, and variscite in 0.2 *N* nitric acid about ten times and makes them almost completely soluble in 12 per cent hydrochloric acid. Peterson (51) conducted similar investigations and showed that heating wavellite for five hours at 200°C. increased the solubility of the phosphoric acid 4 to 50 per cent and heating to 240°C. increased the solubility to 100 per cent. Dufrénite, when heated at 200°C., was but slightly increased in solubility.

*Views concerning the comparative availability of phosphates of aluminum, iron and calcium*

Below we have simply an enumeration of claims and counter-claims as to the comparative values of aluminum, iron and calcium phosphates. Many of the statements decrying the value of aluminum and iron phosphates were based not on experimental work planned to test this particular point, but were the outcome of efforts to explain puzzling irregularities in the behavior of superphosphates and acid phosphates. Very many workers, too, reported on the topic under discussion as a side issue of a large problem and very often such work failed to effect a fair comparison because the individual phosphates probably display their optimum availability under unlike conditions.

Merrill (43) reported that in most cases crude Florida rock phosphate outyielded Redonda phosphate. Paturel (49) advised that lime be applied to soils high in oxides of aluminum to prevent the fixation of phosphorus by them. Morse (44), as has already been pointed out, studied the solubility of aluminum phosphates and the effect of dehydration of them and showed that, while the solubility in neutral ammonium citrate was greatly increased, field tests failed to demonstrate a resulting increase in availability. Hilgard (27), as quoted in a former paragraph, stated that in the presence of high lime percentages, relatively low percentages of phosphoric acid and potash may nevertheless prove adequate. This seems to indicate that Hilgard preferred calcium and magnesium as carriers of the phosphate in the soil to other bases.

Deherain mentioned an experiment in France in which the action of superphosphates was very fleeting, due, supposedly, to the phosphoric acid passing into combination with iron and aluminum and so rendering the phosphate incapable of use as plant-food. Wheeler and Adams (83) predicted that soluble phosphates were not likely to have as good after effects on unlimed soil rich in iron and aluminum oxides as would bone meal and basic slag for the reason that the phosphoric acid would be fixed as aluminum and iron phosphates, in which forms plants cannot secure it readily. Gaither (21) studying the effect of lime on the solubility of soil constituents declared that lime renders the insoluble phosphates in the soil soluble by replacing iron and aluminum, which are in combination with phosphorus.

Pfeiffer and Blanck (53) analyzed the effect of alumina and silicic acid gels on the assimilation of phosphoric acid by plants and obtained results which showed that both gels reduced yields of plants as well as their phosphoric acid content. The experiment was conducted with sand fertilized with 3 gm. of basic potassium phosphate and soil extract.

Bishop (4) worked with soybeans in pot cultures and concluded that soluble phosphates were not more desirable than Florida soft rock, iron and aluminum phosphates. Balentine (3) and later Merrill and Jordan (42), all of the Maine Agricultural Experiment Station working with sand cultures, found that acid phosphate gave the best returns in all cases and especially with the *Graminae*. Redondite, a phosphate or iron and aluminum, gave better results with *Graminae* than rock phosphate, but in all other cases the reverse was true. In the second report when these investigators worked with a larger variety of plants, they stated that acid phosphate was best, but the insoluble forms were utilized to a considerable extent and that Florida rock phosphate, on the whole, was better than iron and aluminum phosphates, except for barley, corn, turnips, and potato tubers. The plants used in the investigation were peas, clover, turnips, ruta-bagas, barley, corn, tomatoes, and potatoes. Andouard (1) worked with a calcareous soil and deduced that aluminum phosphate was readily available to plants. Burkett (7) obtained very favorable results with raw and roasted redondite. Gedroits (22), in pot culture with soil, declared that aluminum phosphate gave better yields than calcium phosphate and the latter better yields than iron phosphate. Director Patterson (50) of the Maryland Agricultural Experiment Station, made the following statement: "The iron and alumina phosphates proved in all cases to be valuable sources of phosphoric acid, and it would seem that they deserve a higher rank as a fertilizer than that usually accorded them."

Nagaoka (45) employed phosphates on rice fields exhausted by continuous cropping. All the phosphates gave large increases in yield. Table 1 gives the relative yields, double superphosphates being taken as 100.

Bonomi (5), in comparing aluminum phosphate with mineral phosphate, superphosphate, and Thomas slag, reported that aluminum phosphate gave large increases in yield with both clover and wheat, but that superphosphate was always superior to it; spring wheat yields with aluminum phosphate was smaller than those with Thomas slag, but with clover the reverse was true. Elliot and Hill (16) showed that from weights of crops produced in pot experiments, iron and aluminum do not fix phosphoric acid in forms unavailable to plants; as a matter of fact, they claim that iron and aluminum phosphates produce more plant growth than the calcium compounds do. For this reason, they denounced the solvents used by chemists for determining the reversion of phosphates as useless for the purpose.

TABLE 1  
*Relative yields of rice as influenced by various phosphates (from Nagaoka)*

	FIRST YEAR	SECOND YEAR	THIRD YEAR	FOURTH YEAR	AVER- AGE
1. Double super phosphate.....	100	100	100	100	100
2. Ferric phosphate.....	140	141	399	58	185
3. Ferrous phosphate.....	87	88	194	44	103
4. Aluminum phosphate.....	92	145	514	103	216
5. Calcium phosphate.....	117	110	161	118	127

Shulov (71) worked with vivianite—a ferrous phosphate—a pure ferrous phosphate, aluminum phosphates, tricalcium phosphate, and superphosphates in sand cultures. In all cases, the iron and aluminum phosphates proved highly efficient as fertilizer and increasing amounts of lime up to 1 per cent produced very little depressing effect on their action. Baguley (2) compared normal orthophosphates of calcium, iron and aluminum on oats, peas, and Swedish turnips grown on artificial soil of sand and chalk. As a general rule, iron and aluminum phosphates proved more efficient than calcium phosphates. Peterson and Truog (52), in pot cultural work, demonstrated that freshly precipitated and dried ferric phosphate served as a better source of phosphorus for oats than did rock phosphate, while for rape, the results were exactly the reverse. Truog (75) later made the following statement: "Contrary to the general belief that aluminum and iron phosphates are relatively unavailable to plants, nine out of ten plants tested made better growth on aluminum phosphate than on calcium phosphate, and six better growth on ferric phosphate."

#### EXPERIMENTAL

These experiments were planned to determine whether or not it is desirable to employ mineral phosphates of aluminum and iron as sources of phosphorus. Studies were made comparing their value as sources of phosphorus with that of calcium phosphate in various forms both natural and artificial. Simultaneously efforts were made to determine what conditions would cause these phosphates to be of the greatest value for crop growth.

#### *Description of materials used*

The aluminum phosphates employed were lazulite from near Death Valley, Inyo county, California, wavellite from Cumberland county, Pennsylvania and Saldanha phosphate from the Cape Province in South Africa; the iron

phosphates were dufrenite from near Vesuvius, Rockbridge county, Virginia; and vivianite from Leadville, Colorado; the calcium phosphates were Florida rock and Laingsburg phosphate from the Cape Province, South Africa. Some of the wavellite was obtained from Montgomery county, Arkansas. Besides these phosphates there were also used bonemeal and acid phosphate. In the sand cultures disodium hydrogen phosphate in solution replaced the acid phosphate. Table 2 gives the analyses of the various phosphates.

TABLE 2  
*Composition of phosphates employed in experiments*

KIND OF PHOSPHATE	PHOSPHORUS	ALUMINUM	IRON	CALCIUM
	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>
Lazulite.....	13.72	16.20	5.04	0.97
Wavellite.....	10.04	17.40	2.48	0.23
Saldanha.....	9.14	16.30	1.61	1.06
Dufrenite.....	12.07	1.60	40.20	0.11
Vivianite.....	9.11	1.20	22.40	0.10
Florida hard rock.....	14.70	4.17	1.53	26.40
Laingsburg.....	14.01	2.92	2.59	31.90
Bonemeal.....	12.52	0.00	Trace	27.10
Acid phosphate.....	7.01	0.81	0.40	14.70

All the aluminum phosphates are basic phosphates, i.e., they have aluminum hydrate associated with the phosphate and all of the phosphates are more or less hydrated. Lazulite has the additional property of being completely insoluble in acids. Hot aqua regia acting on lazulite for an hour fails to dissolve more than a trace of phosphoric acid. Wavellite and Saldanha phos-

TABLE 3  
*Essential plant-food elements per acre of 2,000,000 pounds of water-free soil or approximately the surface layer of 6½ inches over one acre*

PLANT FOOD ELEMENTS	BROWN SILT LOAM	YELLOW SILT LOAM
	<i>lbs.</i>	<i>lbs.</i>
Phosphorus.....	1,096	706
Potassium.....	32,240	29,180
Nitrogen.....	4,287	1,942
Limestone requirement by Hopkins' method in pounds of CaCO <sub>3</sub> per acre.....	400	2,949

phates dissolve readily in acids. Infrenite is a basic ferric phosphate containing a trace of magnesium. The formula usually ascribed to it by geologists is,  $\text{FePO}_4 \cdot \text{Fe}(\text{OH})_3$ . Vivianite crystallizes in the monoclinic form and is a hydrated ferrous phosphate with the formula  $\text{Fe}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$ . The Florida hard rock is rather high in aluminum as compared to the usual run of phosphate from this source. The Laingsburg phosphate contains quite an appreciable quantity of calcium carbonate.

The pot cultures were conducted in 1-gallon glazed earthen-ware pots drained by a hole in the bottom of the pot and capable of holding 10 pounds of soil. In most of the soil cultures a light phase of brown silt loam from the University Farm at Urbana, Illinois, was used. As far as is known the soil had never been cultivated and had never received soil treatment of any kind. The soil is known to respond readily to applications of phosphorus. In later experiments a yellow silt loam soil was introduced. This soil came from near Vienna, in Johnson county, Illinois.

In all soil cultures 10 pounds of soil were used per pot and in the sand cultures 12 pounds of sand.

#### *Experiment 1*

This experiment was planned to test the comparative effects of the phosphates on crops and the effect of lime and gypsum on their availability.

The experiment was begun in the spring of 1920. Brown silt loam was used and treated as described in table 4.

The pots were planted to buckwheat and annual white sweet clover. All the buckwheat pots were numbered as in table 4; the sweet clover pots were given the same numbers as the buckwheat pots but had "x" prefixed to the number. Each treatment was carried out in duplicate. The planting occurred on February 6, 1920. The sweet clover seed was inoculated. Twenty buckwheat seeds and thirty sweet clover seeds were planted in each pot. After the seeds were up the plants were gradually thinned so that at the end of 4 weeks only the seven strongest buckwheat plants were left in each pot and the ten strongest sweet clover plants in each of the sweet clover pots.

Much cloudy weather was experienced and this combined with the short days made growing conditions in the greenhouse unsatisfactory. It was noticed that the buckwheat especially was looking decidedly poor. In order to insure the elimination of all factors tending toward depression of growth it was thought advisable to start a new series of cultures in which the buckwheat would receive an application of 1.84 gm. of calcium nitrate, the equivalent of 100 pounds of nitrogen to the acre. In all other respects the same plan of treatment was followed, also:

Series 600 corresponded exactly with series 100  
Series 700 corresponded exactly with series 200  
Series 800 corresponded exactly with series 300  
Series 900 corresponded exactly with series 400  
Series 1000 corresponded exactly with series 500

In addition, eight control pots were planted to determine the effect of limestone gypsum and calcium nitrate. The treatment applied to these pots and the yields obtained are shown in table 5.

The planting of this series began on February 22, and was completed on February 24.



TABLE 4  
Yields of buckwheat and sweet clover grown on brown silt loam soil treated with various phosphates

PHOSPHORUS		TREATMENT*	NUMBER OF POT	YIELD OF BUCKWHEAT			INCREASE OVER CHECK	NUMBER OF POT	YIELD OF SWEET CLOVER			INCREASE OVER CHECK
Source	Amount			First pot	Second pot	Average			First pot	Second pot	Average	
	gm.			gm.	gm.	gm.	per cent		gm.	gm.	gm.	per cent
Lazulite.....	2.15		Check	9.2	8.9	9.05		Check	8.9	9.9	9.4	
		Nothing	101A	10.5	10.6	10.55	16.6	x101A	8.8	9.5	9.20	-2.1
		Limestone	102A	11.0	11.8	11.40	25.9	x102A	8.9	8.8	8.85	-5.9
		Gypsum	103A	10.5	10.8	10.65	17.8	x103A	8.0	Lost	8.00	-14.9
		Gypsum and limestone	104A	10.3	11.3	10.80	19.3	x104A	8.4	9.5	8.95	-4.8
Wavellite.....	2.81	Nothing	101B	12.0	11.8	11.90	31.5	x101B	10.8	11.1	10.95	16.3
		Limestone	102B	14.0	14.7	14.35	58.6	x102B	11.2	11.9	11.55	22.9
		Gypsum	103B	12.6	11.9	12.25	24.3	x103B	10.9	10.7	10.80	14.9
		Gypsum and limestone	104B	14.7	15.0	14.85	64.1	x104B	10.2	12.0	11.10	18.1
		Nothing	101C	11.0	10.6	10.80	19.3	x101C	9.9	9.9	9.9	5.3
Saldanha.....	3.23	Limestone	102C	13.3	14.0	13.65	50.8	x102C	12.0	12.9	12.45	32.4
		Gypsum	103C	10.8	11.1	10.95	20.9	x103C	10.9	11.7	11.30	2.0
		Gypsum and limestone	104C	13.7	13.4	13.55	49.7	x104C	12.8	13.2	13.00	38.3
		Nothing	201A	9.5	8.8	9.15	1.1	x201A	9.8	9.2	9.5	1.1
		Limestone	202A	8.6	8.9	8.75	-3.2	x202A	9.1	8.2	8.65	-8.0
Dufrenite.....	2.44	Gypsum	203A	9.8	9.2	9.50	5.0	x203A	10.0	8.8	9.45	0.0
		Gypsum and limestone	204A	7.2	9.8	8.50	-6.1	x204A	8.4	9.9	9.14	-2.8



Vivianite.....	3.24	Nothing	201B	15.5	15.0	15.25	68.5	x201B	12.0	11.1	11.55	22.9
		Limestone	202B	15.4	13.5	14.45	59.7	x202B	11.8	10.7	11.25	19.7
		Gypsum	203B	14.5	13.4	13.95	54.1	x203B	13.1	11.9	12.50	33.0
		Gypsum and limestone	204B	13.7	13.7	13.70	51.4	x204B	12.1	10.7	11.40	21.3
Florida hard rock.....	2.01	Nothing	301A	15.0	15.3	15.15	67.4	x301A	13.8	14.9	14.35	52.7
		Limestone	302A	14.9	14.8	14.85	64.1	x302A	15.0	13.7	14.35	52.7
		Gypsum	303A	15.0	14.3	14.65	61.8	x303A	14.6	14.2	14.25	51.6
		Gypsum and limestone	304A	12.3	10.9	11.60	28.2	x304A	13.7	15.0	14.35	52.7
Laingsburg phosphate.....	2.00	Nothing	301B	15.9	17.0	16.45	81.6	x301B	15.3	13.3	14.30	52.1
		Limestone	302B	13.2	12.3	12.75	40.9	x302B	14.8	15.0	14.90	58.5
		Gypsum	303B	13.9	14.4	14.15	56.3	x303B	13.1	16.5	14.80	57.4
		Gypsum and limestone	304B	12.7	12.9	12.80	41.4	x304B	14.2	15.6	14.90	58.5
Bone meal.....	2.24	Nothing	401	18.2	17.6	17.90	97.8	x401	15.4	13.7	14.55	54.8
		Limestone	402	16.4	17.2	16.80	85.6	x402	14.7	15.4	15.05	60.1
		Gypsum	403	20.5	18.0	19.25	113.3	x403	14.5	15.9	15.20	61.7
		Gypsum and limestone	404	15.9	16.0	15.95	76.2	x404	13.6	16.0	14.80	57.4
Acid phosphate.....	3.80	Nothing	501	15.8	17.9	16.85	86.2	x501	15.1	12.9	14.00	48.9
		Limestone	502	16.9	18.4	17.65	95.1	x502	16.0	13.8	14.90	58.5
		Gypsum	503	17.5	19.0	18.50	104.4	x503	15.8	16.6	15.70	67.0
		Gypsum and limestone	504	17.7	18.3	18.00	98.9	x504	14.4	15.7	15.05	60.1

\* Each gallon pot exposed a soil surface of approximately 179,000<sup>1</sup> acre.

Phosphorus was applied at a rate equivalent to 1000 pounds of 65 per cent rock phosphate per acre, i.e., 130 pounds of phosphorus per acre.

Limestone was applied at the rate of 1 ton per acre or 4.35 gm. per pot.

Gypsum was applied at the rate of 200 pounds per acre or 0.45 gm. per pot.

From the third week in February to the end of March good growing weather prevailed. All the plants made good growth. On the following dates the plants were sprayed with nicotine sulfate to kill thrips with which they had become infested: March 7 and 8, April 2, 18 and 19. The spraying on March 7 was done in cloudy weather. The weather, however, suddenly cleared up with the result that some of the plants were injured. "Scald" spots developed on the buckwheat. The 600 series suffered most. On all other occasions spraying was done in the evening. The crops were harvested May 1, preserved in cheesecloth bags until air-dry and weighed.

TABLE 5

*Yields of buckwheat on brown silt loam showing the effect of calcium nitrate limestone and gypsum applied singly and in all possible combinations*

NUMBER OF POT	TREATMENT	YIELD OF CROP			INCREASE OVER CHECK
		First pot	Second pot	Average	
		gm.	gm.	gm.	per cent
1101	Calcium nitrate	10.9	11.7	11.3	28.4
1102	Calcium nitrate, L	11.4	9.9	10.65	22.1
1103	Calcium nitrate, G	11.8	12.0	11.9	35.3
1104	Calcium nitrate, G, L	10.0	10.0	10.0	13.7
1105	L	8.9	8.9	8.9	1.1
1106	G	9.1	8.8	8.95	1.7
1107	G, L	9.4	8.4	8.9	1.1
Check	None	8.7	8.9	8.8	

## DISCUSSION AND RESULTS OF EXPERIMENT 1

The relative increase in yield over checks are significant in all cases except perhaps for lazulite and dufrenite. The yields and increases in yields are recorded in tables 4, 5, and 6.

In table 6 the percentage increase over checks was calculated with pot 1101 as the check. From table 5, the effect of limestone, gypsum and calcium nitrate may be determined. Limestone and gypsum had no apparent effect when applied either alone or in combination. Series 100 to 500 inclusive show that on buckwheat, bonemeal and acid phosphate gave the best results. Large increases in yield were obtained with the mineral phosphates of calcium on the unlimed pots and with wavellite and Saldanha on the limed pots. Vivianite gave substantial increases in yield in both the limed and unlimed soil. The yields with Florida phosphate and Laingsburg phosphate on the limed pots showed that the crops were benefited considerably by the addition of the phosphorus. On the unlimed pots small, but probably significant, increases in yield were obtained where wavellite and Saldanha phosphates were used. Dufrenite and lazulite had little or no effect on the growth of the buckwheat.

From series 600 to 1000, inclusive, the value of calcium nitrate when used in conjunction with the phosphate minerals can be determined. Table 6 shows

TABLE 6

*Yields of buckwheat grown on brown silt loam treated with various phosphates together with calcium nitrate*

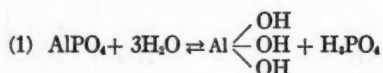
NUMBER OF POT	TREATMENT*	YIELD OF CROPS			INCREASE OVER NO. 1101
		First pot	Second pot	Average	
		gm.	gm.	gm.	per cent
601A	Laz.	14.0	13.7	13.85	22.6
602A	Laz., L	16.2	16.1	16.15	42.9
603A	Laz., G	12.8	13.4	13.10	15.9
604A	Laz., G, L	15.4	16.2	15.80	39.8
601B	Wav.	16.8	16.4	16.60	46.9
602B	Wav., L	20.3	21.4	20.85	84.5
603B	Wav., G	15.9	15.7	15.80	39.8
604B	Wav., G, L	19.4	19.0	19.20	69.9
601C	Sal.	16.1	16.6	16.35	44.7
602C	Sal., L	19.5	19.2	19.35	71.2
603C	Sal., G	16.2	15.3	15.75	39.4
604C	Sal., G, L	19.6	18.1	18.85	66.8
701A	Duf.	15.4	14.9	15.15	34.1
702A	Duf., L	16.5	15.2	15.85	40.3
703A	Duf., G	15.8	15.4	15.60	38.1
704A	Duf., G, L	14.3	14.0	14.15	25.2
701B	Viv.	18.6	18.5	18.55	64.1
702B	Viv., L	17.4	18.0	17.70	56.7
703B	Viv., G	17.6	17.9	17.75	57.1
704B	Viv., G, L	20.2	20.2	20.20	78.7
801A	Fl. R.	18.0	20.4	19.20	69.6
802A	Fl. R., L	18.1	17.9	18.00	59.3
803A	Fl. R., G	19.3	20.6	19.95	76.6
804A	Fl. R., G, L	18.0	17.7	17.85	57.9
801B	Lgg.	20.2	20.9	20.55	81.8
802B	Lgg., L	15.6	16.3	15.95	41.1
803B	Lgg., G	21.2	19.9	20.55	81.8
804B	Lgg., G, L	17.0	16.6	16.80	48.7
901	Bone	20.8	19.7	20.25	79.2
902	Bone, L	16.1	17.1	16.60	46.9
903	Bone, G	18.9	17.9	18.40	62.8
904	Bone, G, L	15.8	16.3	16.05	42.0
1001	Ac. P.	18.8	20.1	19.45	72.1
1002	Ac. P., L	19.0	18.7	18.85	66.8
1003	Ac. P., G	17.9	19.6	18.75	65.9
1004	Ac. P., G, L	19.4	19.4	19.40	71.7

\*These treatments were identically the same as those given in table 4.

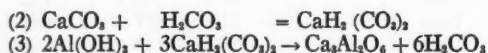
that it enhanced the value of all the phosphates except bonemeal and acid phosphate. Even lazulite and dufrenite in this experiment have benefited the buckwheat considerably. The increases in yield here show that wavellite and Saldanha phosphate on limed soil are on a par with the calcium phosphate minerals on unlimed soil and as good as bonemeal, acid phosphate and vivianite.

With sweet clover different results were obtained. Lazulite and dufrenite again showed no effect. Vivianite gave small but significant increases in yield. On unlimed soil Saldanha phosphate had no effect on crop growth but on the limed soil substantial increases in growth were evident. The best results were obtained with the calcium phosphates. Little difference could be discerned between these phosphates.

It is noticeable that with the aluminum phosphate consistent gains in yield were made by the addition of lime; with the iron phosphate no effect was noticeable, and with calcium phosphates the reverse effect was to be observed. As already pointed out the phosphates of aluminum and iron employed in this experiment are basic phosphates. Aluminum phosphate according to Truog (77) owes its availability to the relative ease with which it hydrolyses in neutral or nearly neutral solutions. From a chemical point of view, this assumption is probably correct. The salt is formed from a strong acid and a weak base and will, therefore, hydrolyze readily according to the following equation:



When such a reaction takes place in the presence of plant roots, there will be a tendency for the phosphoric acid to be removed and the aluminum hydrate to remain in the soil. The net result would be that the aluminum phosphate in the soil will become more and more basic. From the law of mass action it is evident that as the phosphate becomes more basic the rate of hydrolysis of the phosphate will diminish. As time goes on plants will experience increasing difficulty to obtain phosphorus as a result of the reaction represented in equation (1). The beneficial action of lime on aluminum is evident from the following reactions:

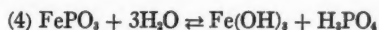


The lime therefore removes the aluminum hydrate from the reaction by precipitating it as the very insoluble calcium aluminate. The continual removal of aluminum hydrate prevents reaction (1) from reaching an equilibrium so that plants will be supplied steadily with a supply of soluble phosphorus. The lime may, of course, precipitate the phosphoric acid as tricalcium phos-

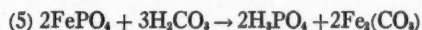
phate but such precipitated tricalcium phosphate has repeatedly been shown to be readily available. The phosphorus will become thoroughly disseminated in the soil and furthermore is readily rendered soluble by carbonic acid in the following manner:



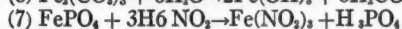
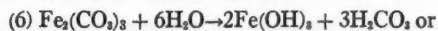
The fact that lime failed to increase the assimilation of ferric phosphate and ferrous phosphate is evident from the above explanation. Iron is a stronger base producing substance than aluminum as is proved by the fact that ferric and ferrous hydrates never behave in the capacity of acids as aluminum hydrate does. Lime, therefore, will have no effect upon ferric or ferrous hydrate. It may be assumed that iron phosphates hydrolyze in the same manner as aluminum phosphates but they are not likely to hydrolyze as readily.



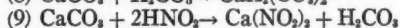
We would have to conclude, therefore, that as the phosphoric acid is used by the plants the residue will always become increasingly basic and unavailable to plants. Vivianite is a fairly pure ferrous phosphate,  $\text{Fe}_3(\text{PO}_4)_2$ ; while dufrénite is a basic ferric phosphate,  $\text{FePO}_4 \cdot \text{Fe}(\text{OH})_3$ . This probably explains in part the greater availability of vivianite. Probably the utilization of iron phosphates by plants in the soil must be explained as being chiefly due to the action of acids, carbonic acid and nitrous acid, both of which are produced in quantity in soils containing a fair amount of organic matter.



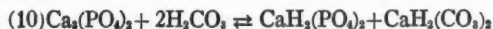
The  $\text{Fe}_2(\text{CO}_3)_3$  is unstable and readily hydrolyzes to give the following:



Chemically, one would expect that the availability of tricalcium phosphate would be suppressed by the action of limestone. Carbonic acid and nitrous acid produced in soil will react in part at least with the limestone.



Apart from this factor the introduction of the common calcium ion will tend to force the equilibrium of the following equation to the left rather than to the right.



Truog (77) was able to demonstrate by pot cultures that the introduction of soluble calcium ions into the soil solution tended to lower the rate of assimilation of phosphorus from tricalcium phosphate. This applies especially to plants which do not feed heavily on calcium.

In the literature survey, Hilgard (27) was quoted as stating that in calcareous soils relatively smaller percentages of phosphoric acid will suffice for good plant growth than in acid soils. Truog (77) referring to observations of a decrease in growth of cereals due to the addition of lime carbonate in pot cultures, makes the following statement

"This decrease in availability is undoubtedly due to a condition which is temporary. In becoming acid a soil goes into a condition which takes years to develop, and the addition of lime carbonate causes many profound changes, some of which may affect the availability of the phosphorus. The very favorable results obtained by investigators in long continued field experiments involving the use of ground limestone is strong evidence that any unfavorable result at the start is due to temporary conditions."

If we consider the fact that in a soil, and even a calcareous soil, there is considerably more aluminum, as a rule, than calcium, we cannot but believe that during the ages of weathering to which soils have been subjected, a considerable quantity of phosphorus has gone into combination with aluminum. This phosphorus will be readily available to plants in a calcareous medium as had already been explained. Is it not the aluminum phosphate in the soil rather than the calcium phosphate that has caused Hilgard to express the opinion quoted above? On the other hand, the favorable results obtained in field experiments as the result of long continued use of limestone may be explained in the following manner. Legumes in general grow better in limed soils. Good farm practice would, therefore, result in the incorporation of more organic matter in the soil and especially of more highly nitrogenous organic matter. The limestone creates conditions favorable for biological activity in the soil. The organic matter is more rapidly decomposed and hence there is rapid production of carbon dioxide and nitrous acid. These acids may readily produce acid zones in the soil. In such a heterogeneous mass as the soil, it is not difficult to conceive of acid and alkaline or neutral zones in close proximity. These zones will naturally not be stationary. Acid zones will continuously be formed and again destroyed. In the acid zones, tricalcium phosphate will be dissolved and rendered available to plants; in the alkaline zones, aluminum phosphates will be hydrolyzed and rendered available to crops so that, even there, soluble phosphorus will not be lacking entirely. Lime, as such, undoubtedly reduces the availability of tricalcium phosphate but due to its effect on the organic matter and on the biological activities of the soil, it acts indirectly as a liberator of phosphorus.

Gypsum was added to certain pots in an endeavour to stimulate root growth in the plants and so improve the feeding capacity of the plants. If an increase was to be expected one would have looked for it in connection with the use of aluminum and iron phosphates. With the calcium phosphates, the introduction of the common ion calcium would result in a reduction of yield according to Truog (77). No such reduction can be said to have been observed. The gypsum seems to have been without effect of any kind. It may be pointed out, too, at this time that the choice of calcium nitrate as a nitrogen fertilizer



was probably unfortunate in that it may have caused a reduction in yields on the calcium phosphate pots, due to the introduction of the common ion calcium. On the other hand the Russian work (10) has shown that calcium nitrate is the best form of nitrogen to apply for buckwheat. It is decidedly superior to sodium nitrate. The use of ammonium salts was avoided since it would have introduced the factor of extremely rapid nitrification and the copious production of acids.

Buckwheat and sweet clover were chosen as crops because of their reputation as strong feeders on insoluble phosphates.

### *Experiment 2*

In order to test the various phosphates under conditions where no soil phosphorus was present it was thought advisable to compare their action in sand culture. Buckwheat and sweet clover were again chosen as the crops to be grown. The phosphates, lime and gypsum were applied by thoroughly mixing them in the sand. The rest of the required plant-food nutrients were added in a culture solution composed of 10 cc. of each of the following solutions and the mixture diluted to a liter.

164	gm. of calcium nitrate in	2500 cc.
50	gm. of potassium sulfate in	2500 cc.
20	gm. of magnesium sulfate in	2500 cc.
0.01	gm. of ferric chloride in	2500 cc.

One liter of nutrient solution was added at the time of planting, another liter after 3 weeks, a third liter 2 weeks later, and thenceforth a liter was applied every week. The same pots were employed as in the former experiment and the same quantities of the phosphates, gypsum, and limestone were employed. Each pot contained 12 pounds of sand. The rate of application of fertilizers were therefore:

Phosphates,	1000 pounds of 65 per cent rock phosphate per acre
Gypsum,	200 pounds per acre
Limestone,	1 ton per acre

The fertilizers applied in the solid form were thoroughly incorporated into the sand.

All the pots were planted in duplicate. The sweet clover pots had an "x" prefixed before each number. The buckwheat pots were planted on March 13, 1920, and harvested on May 13. The sweet clover pots were planted on March 13, 1920, and harvested on May 20. Through an error, one of the pots in the buckwheat series did not receive any phosphorus and had to be discarded.

As in the former experiment 30 seeds were planted in each pot, and as time went on the weaker plants were pulled out until finally the buckwheat pots each contained 7 plants and the sweet clover pots each 10 plants.

On April 2, April 23, and May 4, all the pots were sprayed with nicotine sulfate solution to kill thrips with which the plants had become infested.



TABLE 7  
Treatments applied to various pots

NUMBER OF POT	TREATMENT IN ADDITION TO NUTRIENTS	NUMBER OF POT	TREATMENT IN ADDITION TO NUTRIENTS
1201A	Laz.*	1041A	Fl., R.
1202A	Laz., L	1042A	Fl. R., L
1203A	Laz., G	1403A	Fl. R., G
1204A	Laz., G, L	1404A	Fl. R., G, L
1201B	Wav.	1401B	Lgg.
1202B	Wav., L	1402B	Lgg., L
1203B	Wav., G	1403B	Lgg, G
1204B	Wav., G, L	1404B	Lgg., G, L
1201C	Sal.	1501	Ac. P.
1202C	Sal., L	1502	Ac. P., L
1203C	Sal., G	1503	Ac. P., G
1204C	Sal., G, L	1504	Ac. P., G, L
1301A	Duf.	1601	Bone
1302A	Duf., L	1602	Bone, L
1303A	Duf., G	1603	Bone, G
1304A	Duf., G, L	1604	Bone, G, L
1301B	Viv.		
1302B	Viv., L		
1303B	Viv., G		
1304B	Viv., G, L		

\* For explanation of abbreviations see table 4.

† Included in each liter of nutrient solution at rate of 10 cc. of solution containing 26 gm.  $\text{Na}_2\text{HPO}_4$  in 2500 cc.

#### DISCUSSION AND RESULTS OF EXPERIMENT 2

The weights of the crops produced are recorded in tables 8 and 9.

This experiment bears out even more markedly than the former one the relative ability of buckwheat and sweet clover to assimilate phosphorus from the various sources employed. On the unlimed pots bonemeal was on a par in value to disodium hydrogen phosphate in solution. Vivianite proved to be an excellent source of phosphorus. As in the first experiment, the addition of lime and gypsum had no effect on its availability. The average yield from the vivianite pots was equal to the average yield of all the Florida phosphate and Laingsburg pots. On the unlimed pots the tricalcium phosphate minerals proved superior to vivianite; on the limed pots, inferior. In the buckwheat series, wavellite and Saldanha phosphates in the limed pots were on a par with Florida and Laingsburg phosphates in the unlimed pots. In the sweet clover series this does not hold. The sweet clover made considerably better growth with the aluminum phosphates on the limed pots than on the unlimed pots,

TABLE 8  
Weights of crops of buckwheat produced in sand culture

POT NUMBER	TREATMENT IN ADDITION TO NUTRIENTS	WEIGHT OF CROP			YIELD
		First pot	Second pot	Average	
		gm.	gm.	gm.	per cent pot 1501 = 100 per cent
1201A	Laz.*	1.20	1.20	1.20	7.8
1201B	Wav.	4.76	5.70	5.23	34.2
1201C	Sal.	5.79	5.09	7.44	48.6
1301A	Duf.	2.26	2.14	2.20	14.4
1301B	Viv.	9.77	9.81	9.79	64.0
1401A	Fl. R.	9.23	9.40	9.32	60.9
1401B	Lgg.	12.66	10.44	11.55	75.6
1501	Ac. P.	14.87	15.72	15.30	100.0
1601	Bone	15.02	15.47	15.25	99.7
					per cent pot 1502 = 100 per cent
1202A	Laz., limestone	1.46	1.38	1.42	9.5
1202B	Wav., limestone	9.45	9.98	9.72	65.1
1202C	Sal., limestone	9.49	8.92	9.21	61.7
1302A	Duf., limestone	2.17	2.26	2.23	14.9
1302B	Viv., limestone	9.42	10.04	9.73	65.2
1402B	Fl. R., limestone	6.39	6.97	6.68	44.7
1402B	Lgg., limestone	6.00	6.73	6.37	42.7
1502	Ac. P., limestone	14.93		14.93	100.0
1602	Bone, limestone	12.19	11.49	11.84	79.9
					per cent pot 1503 = 100 per cent
1203A	Laz., gypsum	1.17	1.23	1.20	8.0
1203B	Wav., gypsum	5.69	6.31	6.00	40.3
1203C	Sal., gypsum	5.63	5.40	5.52	36.9
1303A	Duf., gypsum	2.12	2.28	2.20	14.7
1303B	Viv., gypsum	10.01	9.39	9.70	64.9
1403A	Fl. R., gypsum	10.59	11.03	10.81	72.3
1403B	Lgg., gypsum	10.10	11.50	10.80	72.2
1503	Ac. P., gypsum	14.71	15.18	14.95	100.0
1603	Bone, gypsum	14.37	13.65	14.01	93.6
					per cent pot 1504 = 100 per cent
1204A	Laz., limestone, gypsum	1.39	1.55	1.47	9.6
1204B	Wav., limestone, gypsum	9.47	10.16	9.82	64.4
1204C	Sal., limestone, gypsum	10.37	9.09	9.73	63.8
1304A	Duf., limestone, gypsum	2.01	2.41	2.21	14.5
1304B	Viv., limestone, gypsum	10.40	11.29	10.85	71.2
1404A	Fl. R., limestone, gypsum	6.24	6.73	6.49	42.6
1404B	Lgg., limestone, gypsum	6.16	5.80	5.98	39.2
1504	Ac. P., limestone, gypsum	15.81	14.66	15.24	100.0
1604	Bone, limestone, gypsum	11.60	9.18	10.39	68.2

\* For explanation of abbreviations see table 4.

TABLE 9  
Weights of crops of sweet clover produced in sand cultures

POT NUMBER	TREATMENT IN ADDITION TO NUTRIENTS	WEIGHT OF CROPS			YIELD
		First pot	Second pot	Average	
		gm.	gm.	gm.	per cent pot x1501 = 100 per cent
x1201A	Laz.*	2.18	2.29	2.24	19.7
x1201B	Wav.	2.51	2.61	2.56	22.5
x1201C	Sal.	2.6	2.86	2.73	24.0
x1301A	Duf.	2.40	2.11	2.31	20.3
x1301B	Viv.	8.53	9.82	9.18	80.8
x1401A	Fl. R.	10.37	10.54	10.46	92.1
x1401B	Lgg.	10.13	10.06	10.15	89.3
x1501	Ac. P.	11.74	10.98	11.36	100.0
x1601	Bone	12.53	13.02	12.78	112.5
					per cent pot x1502 = 100 per cent
x1202A	Laz. limestone	3.01	3.10	3.56	26.6
x1202B	Wav., limestone	6.72	6.50	6.61	49.4
x1202C	Sal., limestone	7.35	7.38	7.37	55.0
x1302A	Duf., limestone	2.26	2.09	2.18	16.3
x1302B	Viv., limestone	9.20	8.41	8.81	65.8
x1402A	Fl. R., limestone	8.63	8.40	8.52	63.6
x1402B	Lgg., limestone	7.31	7.74	7.53	56.2
x1502	Ac. P., limestone	13.42	13.36	13.39	100.0
x1602	Bone, limestone	10.19	10.42	10.31	76.9
					per cent pot x1503 = 100 per cent
x1203A	Laz., gypsum	2.00	1.92	1.96	15.6
x1203B	Wav., gypsum	3.14	2.89	3.02	24.1
x1203C	Sal., gypsum	2.67	2.81	2.74	21.9
x1303A	Duf., gypsum	2.37	2.17	2.27	18.1
x1303B	Viv., gypsum	10.54	9.18	9.86	78.6
x1403A	Fl. R., gypsum	12.04	11.09	11.57	92.3
x1403B	Lgg., gypsum	9.68	9.71	9.70	77.4
x1502	Ac. P., gypsum	12.61	12.47	12.54	100.0
x1602	Bone, gypsum	13.35	12.72	13.04	103.9
					per cent pot x1504 = 100 per cent
x1204A	Laz., limestone, gypsum	2.98	2.89	2.93	21.8
x1204B	Wav., limestone, gypsum	6.71	7.22	6.97	51.9
x1204C	Sal., limestone, gypsum	8.13	8.17	8.15	60.7
x1304A	Duf., limestone, gypsum	2.42	2.27	2.35	17.5
x1304B	Viv., limestone, gypsum	9.79	9.81	9.80	73.0
x1404A	Fl.R., limestone, gypsum	8.86	8.28	8.57	63.9
x1404B	Lgg., limestone, gypsum	6.80	7.45	7.13	53.1
x1504	Ac.P. limestone, gypsum	13.29	13.54	13.42	100.0
x1604	Bone, limestone, gypsum	10.01	10.76	10.39	77.4

\* For explanation of abbreviations see Table 4.

but the yields were not as large as those obtained on the unlimed pots fertilized with the tricalcium phosphate minerals. The Florida and Laingsburg phosphates, as with the buckwheat, proved inferior in the limed pots to the same phosphates in the unlimed pots, but in this case equally as good as wavelite and Saldanha on the limed pots. Lazulite and dufrénite behaved as they did in the first experiment, proving themselves poor sources of phosphorus.

A fact to be recorded and probably of some significance is that in the earlier stages of growth of the buckwheat the big differences in total growth on the aluminum phosphate were not so much in evidence. It was during the last 4 or 5 weeks of growth that the plants on the limed pots displayed a greater rate of growth than those on the unlimed pots. Plate 1, figure 1, shows the buckwheat at the age of 6 weeks. The effects of liming is plainly evident where the calcium minerals were applied but not nearly so well marked where aluminum minerals were used. Figure 2 shows that where sweet clover was grown liming showed very marked influence from the very beginning. The pot marked  $\alpha 1705$  was one of a series that was discarded because of the series becoming infected with red spider. This pot received a complete nutrient solution in which the phosphorus was supplied in the form of monocalcium phosphate. Besides this the pot was limed and treated with 14 gm. of Florida rock phosphate, i.e., rock phosphate at the rate of 7 tons per acre.

These observations tally with the explanation as to assimilability of the phosphates of aluminum and calcium, i.e., in an unlimed medium the availability of aluminum phosphate will decrease as time goes on, whereas the effect of lime on the calcium phosphates will be in evidence immediately. This is considered strong evidence in favor of the explanation as to the effect of lime on the availability of aluminum phosphate.

It is remarkable that similar results have been obtained with buckwheat and sweet clover. Both crops, of course, are known to be heavy feeders on phosphates; but, on the one hand, buckwheat has a rather limited rooting system while sweet clover, on the other hand, has a very extensive rooting system. It seems, therefore, that the two plants should vary considerably in feeding power or else in the manner in which they feed. It is possible to conceive of the idea that the sweet clover may have been injured by aluminum on the aluminum phosphate series. Soluble aluminum in any form would be injurious to sweet clover. This perhaps explains why sweet clover did not respond as well as buckwheat to treatment with aluminum phosphate. Sweet clover roots probably excrete more carbonic acid than do buckwheat roots. Aluminum phosphate is not as readily dissolved by carbonic acid as is tricalcium phosphate. Buckwheat may feed more heavily on phosphorus rendered soluble by hydrolysis by reason of a more rapid removal of phosphorus from the root-hairs to the growing parts of the plant. It must be borne in mind that in these sand cultures, microorganisms do not play the part that they do in soils. None of the pots were inoculated with soil infusion and no nitrifiable material was added. In all probability all pots were infected with

some kind or kinds of organisms but it is not likely that any organisms that could affect the availability of phosphorus appreciably could have been present, or even if they had been present could have exerted any influence, so that the plants had to obtain phosphorus by one of the following methods:

1. The solution of phosphates in the nutrient medium.
2. By hydrolysis and consequent solution of phosphates.
3. By solvent effect of acid root excretions, which would be, according to Czapek (13), chiefly through the agency of carbonic acid.

Phosphorus brought into solution by the first two methods should be equally available to both crops. The phosphorus obtained by the third method would depend on the individuality of the crop in regard to the quantity of the carbonic acid excreted. The differences in feeding power between the two crops under the conditions of the experiment would in all probability have to be ascribed to the rate of carbonic acid excretion, unless there is a difference between the plants in the rate at which phosphorus is translocated from the root hairs to the growing parts of the plants.

It was thought that in sand culture we would be able to duplicate Truog's (77) results with regard to the effect of soluble calcium salts on the availability of the tricalcium phosphate minerals (i.e., reduce it); but gypsum, as in soil cultures, appeared to have no effect on the growth of the plants. It is, of course, possible that due to the large excess of calcium already present in the form of calcium nitrate the additional effect of the calcium ions from the gypsum was too small to register an appreciable difference in crop growth.

### *Experiment 3*

The purpose of this experiment was to determine the effect of nitrification of urea on the availability of the various phosphates both in soil and sand cultures.

The experiment was commenced in the fall of 1920. The media for growth employed were the brown silt loam and the yellow silt loam described in the first section of this paper and pure quartz sand. Throughout the experiment phosphorus and limestone were applied in the same quantities as in former experiments. In the case of the sand cultures the nutrient was applied at the same rate as in previous sand cultures. Where the pots received urea, 0.75 gm. was applied to each pot, i.e., such a quantity was added that, if all the nitrogen in it were converted to nitric acid, enough acid would be formed to displace exactly all the phosphoric acid from the tricalcium phosphate applied to each of the pots treated with it. The pots, which did not receive urea, received an application of 2.05 gm. of calcium nitrate, i.e., nitrogen in equal quantity to that added to the pots receiving urea.

The treatments were applied to all the pots and water added to the optimum amount in each pot. The sand pots each received 50 cc. of a soil infusion. The pots were then left unplanted for 14 days, the object being to allow the urea to be nitrified before the germination of the seed.

TABLE 10  
Treatments applied to individual pots

TREATMENT	BROWN SILT LOAM SERIES POT NUMBERS	YELLOW SILT LOAM SERIES POT NUMBERS	SAND CULTURE SERIES POT NUMBERS
Laz., Ca(NO <sub>3</sub> ) <sub>2</sub> *	11A	61A	111A
Laz., Ca(NO <sub>3</sub> ) <sub>2</sub> , L	12A	62A	112A
Laz., urea	13A	63A	113A
Laz., urea, L	14A	64A	114A
Wav., Ca(NO <sub>3</sub> ) <sub>2</sub>	11B	61B	111B
Wav., Ca(NO <sub>3</sub> ) <sub>2</sub> , L	12B	62B	112B
Wav., urea	13B	63B	113B
Wav., urea, L	14B	64B	114B
Sal., Ca(NO <sub>3</sub> ) <sub>2</sub>	11C	61C	111C
Sal., Ca(NO <sub>3</sub> ) <sub>2</sub> , L	12C	62C	112C
Sal., urea	13C	63C	113C
Sal., urea, L	14C	64C	114C
Duf., Ca(NO <sub>3</sub> ) <sub>2</sub>	21	71	121
Duf., Ca(NO <sub>3</sub> ) <sub>2</sub> , L	22	72	122
Duf., urea	23	73	123
Duf., urea, L	24	74	124
Fl. R., Ca(NO <sub>3</sub> ) <sub>2</sub>	31A	81A	131A
Fl. R., Ca(NO <sub>3</sub> ) <sub>2</sub> , L	32A	82A	132A
Fl. R., urea	33A	83A	133A
Fl. R., urea, L	34A	84A	134A
Lgg., Ca(NO <sub>3</sub> ) <sub>2</sub>	31B	81B	131B
Lgg., Ca(NO <sub>3</sub> ) <sub>2</sub> , L	32B	82B	132B
Lgg., urea	33B	83B	133B
Lgg., urea, L	34B	84B	134B
Bone, Ca(NO <sub>3</sub> ) <sub>2</sub>	41	91	141
Bone, Ca(NO <sub>3</sub> ) <sub>2</sub> , L	42	92	142
Bone, urea	43	93	143
Bone, urea, L	44	94	144
Ac. P., Ca(NO <sub>3</sub> ) <sub>2</sub>	51	101	151
Ac. P., Ca(NO <sub>3</sub> ) <sub>2</sub> , L	52	102	152
Ac. P., urea	53	103	153
Ac. P., urea, L	54	104	154
Ca(NO <sub>3</sub> ) <sub>2</sub>	Check 1	Check 1	No check group
Ca(NO <sub>3</sub> ) <sub>2</sub> , L	" 2	" 2	
Urea	" 3	" 3	
Urea, L	" 4	" 4	

\* For explanation of abbreviations see table 4.

The materials added to the pots were ground together in a mortar and thoroughly mixed before they were incorporated in the growing media. Thorough mixing of the media and the material was effected.

Five series of pots were used, two containing brown silt loam, one containing yellow silt loam, and two containing sand. For each soil, one series was planted to wheat. The two extra series were planted to annual white sweet clover and each of these pots was numbered the same as its corresponding wheat pot except for an "x" prefixed to the number. The pots in the sand series each received in addition a nutrient solution containing magnesium sulfate, potassium sulfate, and ferric chloride. The concentrations of the salts in this solution, the manner and time of application are exactly as described under experiment 1. The treatments applied to the individual pots in all the series are indicated in table 10.

Sweet clover pots in the first series were planted on October 25 and 26, 1920; the wheat pots, on October 27 and 28, 1920; and a second series of pots containing sand were planted to annual white sweet clover on November 7, 1920.

#### DISCUSSION AND RESULTS OF EXPERIMENT 3

Due to poor light conditions during the winter months all the plants made very slow growth so that harvesting occurred only toward the middle of March. During the growing season the greenhouses were fumigated on two occasions with "nicofume" to rid the plants of aphids. On three separate occasions spraying with nicotine sulfate was resorted to in order to kill the thrips with which the plants had become infested. The last 6 weeks of the growing periods when the days were becoming longer the plants grew most rapidly. The sweet clover, especially, remained stunted to a considerable extent in the earlier growing period.

On March 4, the wheat on the sand cultures was harvested. On March 13 and 14, the wheat on the soil cultures was harvested and on March 18, all the sweet clover pots were harvested. The crops were kept in paper bags dried in an oven at 105°C. and weighed.

The weights of crops obtained are recorded in tables 11, 12, 13, 14, and 15.

From the above tables the percentage increase in growth as a result of the treatments can be determined. In general, the yields from the pots not treated with urea substantiate the findings of the first experiment with respect to the comparative availability of the various phosphates and the effect of lime on the assimilability of the phosphorus. With wheat, acid phosphate gave easily the best results on both limed and unlimed soil, while wavellite and Saldanha phosphates on limed soil and bonemeal on unlimed soil were second in their effect. Florida rock and Laingsburg phosphates were effective on the unlimed soil but failed to produce much increased growth on the limed pots. The sweet clover yields on the brown silt loam series showed that, even where pots had been limed, the tricalcium phosphates were a better source of phos-



TABLE 11  
*Weight of wheat from brown silt loam series*

POT NUMBER	TREATMENT	YIELD OF CROP			INCREASE OVER CHECK 1	
		First pot	Second pot	Average		
		gm.	gm.	gm.	per cent	
11A		5.63	5.73	5.68	-1.6	
11B	Wav., $\text{Ca}(\text{NO}_3)_2$	6.68	6.20	6.53	13.2	
11C	Sal., $\text{Ca}(\text{NO}_3)_2$	7.57	8.42	7.99	38.3	
21	Duf., $\text{Ca}(\text{NO}_3)_2$	5.67	5.58	5.63	-2.4	
31A	Fl. R., $\text{Ca}(\text{NO}_3)_2$	8.37	8.92	8.65	49.9	
31B	Lgg., $\text{Ca}(\text{NO}_3)_2$	8.69	8.31	8.50	47.3	
41	Bone, $\text{Ca}(\text{NO}_3)_2$	9.57	9.07	9.32	61.5	
51	Ac. P., $\text{Ca}(\text{NO}_3)_2$	10.72	10.31	10.52	82.3	
Check 1	$\text{Ca}(\text{NO}_3)_2$ alone	5.73	5.81	5.72		
					INCREASE OVER CHECK 2	
					per cent	
12A	Laz., $\text{Ca}(\text{NO}_3)_2$ , L	6.32	6.41	6.37	10.4	13.6
12B	Wav., $\text{Ca}(\text{NO}_3)_2$ , L	8.64	9.42	9.03	56.5	61.5
12C	Sal., $\text{Ca}(\text{NO}_3)_2$ , L	8.57	9.42	9.00	56.3	61.0
22	Duf., $\text{Ca}(\text{NO}_3)_2$ , L	5.71	5.46	5.59	-3.1	0
32A	Fl. R., $\text{Ca}(\text{NO}_3)_2$ , L	7.09	7.17	7.13	23.6	27.5
32B	Lgg., $\text{Ca}(\text{NO}_3)_2$ , L	6.23	6.26	6.25	8.3	11.8
42	Bone., $\text{Ca}(\text{NO}_3)_2$ , L	8.18	7.84	8.01	38.8	43.3
52	Ac. P., $\text{Ca}(\text{NO}_3)_2$ , L	10.03	10.67	10.35	79.4	85.2
Check 2	$\text{Ca}(\text{NO}_3)_2$ , L	5.71	5.46	5.59	-3.1	
					INCREASE OVER CHECK 3	
					per cent	
13A	Laz., urea	12.80	13.27	13.04	125.9	25.0
13B	Wav., urea	14.95	14.15	14.55	152.2	39.5
13C	Sal., urea	14.71	15.88	15.30	165.1	46.7
23	Duf., urea	13.69	15.31	14.50	153.2	39.0
33A	Fl. R., urea	20.82	19.70	20.26	251.1	94.2
33B	Lgg., urea	19.68	19.97	19.83	243.7	90.1
43	Bone, urea	18.50	19.82	19.16	232.1	83.7
53	Ac. P., urea	16.41	16.84	16.63	188.2	59.5
Check 3	Urea alone	10.09	10.77	10.43	80.7	
					INCREASE OVER CHECK 4	
					per cent	
14A	Laz., urea, L	10.73	10.75	10.74	86.3	23.6
14B	Wav., urea, L	10.96	12.00	11.48	98.9	31.9
14C	Sal., urea, L	11.74	12.54	12.14	110.4	39.7
24	Duf., urea, L	12.07	11.42	11.80	104.5	35.7
24A	Fl. R., urea, L	17.76	16.55	17.16	197.4	97.5
34B	Lgg., urea, L	14.80	14.03	14.42	149.9	65.9
44	Bone, urea, L	17.25	16.80	17.03	195.1	95.9
54	Ac. P., urea, L	15.35	15.24	15.30	165.2	76.1
Check 4	Urea, L	8.48	8.89	8.69	50.6	

TABLE 12  
*Yields of sweet clover from brown silt loam soil series*

POT NUMBER	TREATMENT	YIELD OF CROA			INCREASE OVER X CHECK 1	
		First pot	Second pot	Average		
		gm.	gm.	gm.	per cent	
x11A	Laz., $\text{Ca}(\text{NO}_3)_2$	4.78	4.41	4.60	-3.4	
x11B	Wav., $\text{Ca}(\text{NO}_3)_2$	5.44	5.70	5.57	17.0	
x11C	Sal., $\text{Ca}(\text{NO}_3)_2$	4.65	5.48	5.06	6.3	
x21	Duf., $\text{Ca}(\text{NO}_3)_2$	4.70	5.47	5.09	6.9	
x31A	Fl. R., $\text{Ca}(\text{NO}_3)_2$	7.93	7.15	7.54	58.4	
x31B	Lgg., $\text{Ca}(\text{NO}_3)_2$	7.46	7.26	7.36	54.6	
x41	Bone, $\text{Ca}(\text{NO}_3)_2$	10.57	9.66	10.12	112.6	
x51	Ac. P., $\text{Ca}(\text{NO}_3)_2$	6.72	7.90	7.31	53.6	
xCheck 1	$\text{Ca}(\text{NO}_3)_2$ , alone	4.80	4.22	4.76		
					INCREASE OVER X CHECK 2	
					per cent	
x12A	Laz., $\text{Ca}(\text{NO}_3)_2$ , L	5.45	4.95	5.20	9.5	-0.4
x12B	Wav., $\text{Ca}(\text{NO}_3)_2$ , L	6.00	6.46	6.23	30.9	19.3
x12C	Sal., $\text{Ca}(\text{NO}_3)_2$ , L	6.84	6.13	6.49	36.3	24.3
x22	Duf., $\text{Ca}(\text{NO}_3)_2$ , L	5.44	5.31	5.38	13.0	3.1
x32A	Fl. R., $\text{Ca}(\text{NO}_3)_2$ , L	6.68	7.05	6.87	44.3	31.6
x32B	Lgg., $\text{Ca}(\text{NO}_3)_2$ , L	6.70	6.23	6.47	35.9	23.9
x42	Bone, $\text{Ca}(\text{NO}_3)_2$ , L	8.70	7.80	8.25	73.3	58.0
x52	Ac. P., $\text{Ca}(\text{NO}_3)_2$ , L	10.69	9.56	10.13	112.8	94.1
xCheck 2	$\text{Ca}(\text{NO}_3)_2$ , L	5.12	5.32	5.22	9.7	
					INCREASE OVER X CHECK 3	
					per cent	
x13A	Laz., urea	4.87	4.53	4.70	-1.3	13.3
x13B	Wav., urea	5.62	6.21	5.92	24.4	42.7
x13C	Sal., urea	5.11	5.24	5.18	8.8	27.2
x23	Duf., urea	7.21	6.80	7.01	47.3	68.9
x33A	Fl. R., urea	8.12	8.37	8.25	73.3	98.8
x33B	Lgg., urea	6.24	7.67	6.96	46.2	67.7
x43	Bone, urea	7.33	8.03	7.68	61.3	85.1
x53	Ac. P., urea	7.55	7.23	7.39	55.3	33.3
xCheck 3	Urea alone	4.38	3.92	4.15	-12.8	
					INCREASE OVER X CHECK 4	
					per cent	
x14A	Laz., urea, L	6.72	5.91	6.41	34.7	19.1
x14B	Wav., urea, L	7.34	6.30	6.82	43.3	26.8
x14C	Sal., urea, L	6.73	6.92	6.83	43.3	26.8
x24	Duf., urea, L	6.24	6.42	6.33	32.9	17.7
x34A	Fl. R., urea, L	9.64	8.99	9.33	96.0	73.4
x34B	Lgg., urea, L	9.67	8.94	9.31	95.6	73.1
x44	Bone, urea, L	9.90	10.86	9.38	97.1	74.4
x54	Ac. P., urea, L	10.89	11.74	11.32	137.8	110.4
xCheck 4	Urea, L.	5.29	5.47	5.38	13.0	

phorus for this plant than aluminum and iron phosphates. The effect of liming was concordant with the former findings; it was in the relative powers of assimilating the various phosphates that the plants differed. Wheat uses aluminum phosphates more readily than does sweet clover. Sweet clover is a heavy

TABLE 13

*Yields of wheat from pots in yellow silt loam series. (A large number of crops were lost due to the oven, in which they were being dried, becoming overheated and crops being charred)*

POT NUMBER	TREATMENT	YIELD OF CROPS			INCREASE OVER CHECK 1	
		First pot	Second pot	Average		
		gm.	gm.	gm.	per cent	
61A	Laz., $\text{Ca}(\text{NO}_3)_2$	5.36	4.87	5.12	-1.2	
61B	Wav., $\text{Ca}(\text{NO}_3)_2$	7.48	7.11	7.30	40.8	
61C	Sal., $\text{Ca}(\text{NO}_3)_2$	5.87	5.63	5.75	11.0	
81B	Lgg., $\text{Ca}(\text{NO}_3)_2$	7.23	7.11	7.17	38.4	
Check 1	$\text{Ca}(\text{NO}_3)_2$ , alone	5.18		5.18		
						INCREASE OVER CHECK 2
						per cent
62A	Laz., $\text{Ca}(\text{NO}_3)_2$ , L	6.12	5.85	5.98	15.4	2.9
62B	Wav., $\text{Ca}(\text{NO}_3)_2$ , L	7.37	9.05	8.21	58.5	41.3
62C	Sal., $\text{Ca}(\text{NO}_3)_2$ , L	8.75	8.44	8.60	66.0	48.0
82B	Lgg., $\text{Ca}(\text{NO}_3)_2$ , L	6.40	5.90	6.15	18.7	5.9
Check 2	$\text{Ca}(\text{NO}_3)_2$ , L	5.81		5.81	12.2	
						INCREASE OVER CHECK 3
						per cent
63A	Laz., urea	6.14	6.29	6.22	20.1	0.2
63B	Wav., urea	6.35	6.53	6.44	24.3	3.7
63C	Sal., urea	7.89	10.22	9.06	74.9	45.9
83B	Lgg., urea	9.10	10.07	9.59	85.1	54.4
Check 3	Urea alone	6.21		6.21	20.0	
						INCREASE OVER CHECK 4
						per cent
64A	Laz., urea, L	8.26	7.71	7.99	54.2	30.1
64B	Wav., urea, L	9.69	8.44	9.07	75.1	47.5
64C	Sal., urea, L	10.07	10.35	10.21	97.1	49.8
84B	Lgg., urea, L	8.42	7.97	8.20	58.4	33.5
Check 4	Urea, L	5.92	6.31	6.12	18.1	

feeder on calcium, wheat a light feeder. It is to be expected, therefore, that in the presence of lime or even in the absence of lime sweet clover would be capable of assimilating the phosphorus of tricalcium phosphate more readily than would wheat. Truog (77) is of the opinion that oats feed heavily on the natural phosphates of the soil because of their large fibrous root system.

Wheat, which is very similar to oats in its general structure and manner of feeding, should therefore also feed heavily on soil phosphorus. The results of

TABLE 14  
*Yields of wheat from pots in the sand series*

POT NUMBER	TREATMENT IN ADDITION TO NUTRIENT SOLUTION	YIELD OF CROP		
		First pot	Second pot	Average
		gm.	gm.	gm.
111A	Laz., $\text{Ca}(\text{NO}_3)_2$	1.90	1.28	1.59
111B	Wav., $\text{Ca}(\text{NO}_3)_2$	3.66	4.05	3.86
111C	Sal., $\text{Ca}(\text{NO}_3)_2$	3.16	2.22	2.69
121	Duf., $\text{Ca}(\text{NO}_3)_2$	1.72	2.04	1.88
131A	Fl. R., $\text{Ca}(\text{NO}_3)_2$	2.00	1.95	1.98
131B	Lgg., $\text{Ca}(\text{NO}_3)_2$	2.18	2.07	2.13
141	Bone, $\text{Ca}(\text{NO}_3)_2$	3.11	2.26	2.69
151	Ac. P., $\text{Ca}(\text{NO}_3)_2$	10.04	20.21	19.63
112A	Laz., $\text{Ca}(\text{NO}_3)_2$ , L	1.53	1.31	1.42
112B	Wav., $\text{Ca}(\text{NO}_3)_2$ , L	5.40	5.01	5.21
112C	Sal., $\text{Ca}(\text{NO}_3)_2$ , L	4.06	4.16	4.11
122	Duf., $\text{Ca}(\text{NO}_3)_2$ , L	2.23	2.04	2.14
132A	Fl. R., $\text{Ca}(\text{NO}_3)_2$ , L	1.65	1.54	1.60
132B	Lgg., $\text{Ca}(\text{NO}_3)_2$ , L	2.30	2.12	2.21
142	Bone, $\text{Ca}(\text{NO}_3)_2$ , L	2.38	2.16	2.27
152	Ac. P., $\text{Ca}(\text{NO}_3)_2$ , L	17.62	19.40	18.51
113A	Laz., urea	1.60	2.10	1.85
113B	Wav., urea	4.89	5.21	5.05
113C	Sal., urea	6.01	6.00	6.01
123	Duf., urea	2.46	2.67	2.57
133A	Fl. R., urea	4.30	5.44	4.87
133B	Lgg., urea	4.19	3.90	4.05
143	Bone, urea	7.58		7.58*
153	Ac. P., urea	19.34	20.02	19.68
114A	Laz., urea, L	1.90	1.25	1.58
114B	Wav., urea, L	4.77	5.02	4.90
114C	Sal., urea, L	6.20	6.25	6.23
124	Duf., urea, L	1.64	2.00	1.82
134A	Fl. R., urea, L		2.22	2.22*
134B	Lgg., urea, L	2.40	2.30	2.35
144	Bone, urea, L	2.68		2.68*
154	Ac. P., urea, L	19.59	19.97	19.78

\* Weights from only one pot available. The duplicate plants had died soon after germination, presumably from the toxic effect of either the urea or ammonia formed from it.

the above experiments justify his conclusions, for the wheat grown in sand culture made but poor growth. On the other hand, the wheat has responded very markedly to phosphate treatment on the soils. It seems logical to be-

lieve that the more rapid development of a root system in the soil due to the presence of some readily available phosphorus accounts for the greater ability

TABLE 15  
*Yields of sweet clover from the sand series*

POT NUMBER	TREATMENT IN ADDITION TO NUTRIENT SOLUTION		YIELD OF CROP		
			First pot	Second pot	Average
			gm.	gm.	gm.
x111A	Laz.,	Ca(NO <sub>3</sub> ) <sub>2</sub>	0.84	0.53	0.69
x111B	Wav.,	Ca(NO <sub>3</sub> ) <sub>2</sub>	4.00	5.20	4.60
x111C	Sal.,	Ca(NO <sub>3</sub> ) <sub>2</sub>	5.26	5.53	5.40
x121	Duf.,	Ca(NO <sub>3</sub> ) <sub>2</sub>	1.33	1.03	1.18
x131A	Fl. R.,	Ca(NO <sub>3</sub> ) <sub>2</sub>	7.86	10.23	9.05
x131B	Lgg.,	Ca(NO <sub>3</sub> ) <sub>2</sub>	9.90	9.73	9.82
x141	Bone,	Ca(NO <sub>3</sub> ) <sub>2</sub>	10.27	9.97	10.12
x151	Ac. P.,	Ca(NO <sub>3</sub> ) <sub>2</sub>	11.46	10.17	10.82
x112A	Laz.,	Ca(NO <sub>3</sub> ) <sub>2</sub> , L	1.19	1.14	1.17
x112B	Wav.,	Ca(NO <sub>3</sub> ) <sub>2</sub> , L	6.22	6.10	6.16
x112C	Sal.,	Ca(NO <sub>3</sub> ) <sub>2</sub> , L	6.20	7.93	7.07
x122	Duf.,	Ca(NO <sub>3</sub> ) <sub>2</sub> , L	1.00	1.03	1.02
x132A	Fl. R.,	Ca(NO <sub>3</sub> ) <sub>2</sub> , L	8.23	9.35	8.79
x132B	Lgg.,	Ca(NO <sub>3</sub> ) <sub>2</sub> , L	7.73	7.05	7.39
x142	Bone,	Ca(NO <sub>3</sub> ) <sub>2</sub> , L	7.20	7.04	7.12
x152	Ac. P.,	Ca(NO <sub>3</sub> ) <sub>2</sub> , L	11.57	10.84	11.21
x113A	Laz.,	urea	0.48*	0.12*	
x113B	Wav.,	urea	0.56*	0.77*	
x113C	Sal.,	urea	*	*	
x123	Duf.,	urea	*	*	
x133A	Fl. R.,	urea	7.62	*	
x133B	Lgg.,	urea	8.45	9.39	8.92
x143	Bone,	urea	10.49	*	10.49†
x153	Ac. P.,	urea	7.42	4.32*	7.42†
x114A	Laz.,	urea, L	1.12	1.43	1.28
x114B	Wav.,	urea, L	3.24	3.54	3.39
x114C	Sal.,	urea, L	4.84	5.46	5.15
x124	Duf.,	urea, L	*	1.79	1.79†
x134A	Fl. R.,	urea, L	*	*	
x134B	Lgg.,	urea, L	9.27	8.04	8.66
x144	Bone,	urea, L	8.38	*	8.38†
x154	Ac. P.,	urea, L	11.70	10.92	11.31

\* Part or all of plants died within first 3 weeks.

† From one pot only.

to use phosphorus applied to soil. The poor growth in sand cultures, where only insoluble mineral phosphates are present, is due to the inability to develop a root system in the early growth stages. Sweet clover, with its high

feeding capacity for calcium, finds enough phosphorus in early stages of growth to develop an extensive root system; and, therefore, in later stages is better equipped to forage for its phosphorus. Sweet clover, of course, always has a very much more extensive root system than wheat. The comparison would be more plain if we could compare buckwheat and wheat. It must be borne in mind, however, that the application of calcium nitrate may have reduced the availability of phosphorus for wheat more than for clover, which is capable of utilizing more calcium. It would be interesting to grow wheat in sand culture with insoluble phosphates and supplying it with a very small quantity of soluble phosphorus just after the germination of the plants.

#### THE ACTION OF UREA

Some remarkable results have been obtained as a result of the action of urea. The object of the addition of urea was to determine the effect of nitrification on the availability of the phosphates. It was an ideal source of organic matter to use because of its being free from phosphorus and convertible only into nitrous (or nitric) and carbonic acids, thus leaving no mineral residue in the soil. Furthermore, urea is nitrified very rapidly. The urea is converted into ammonium carbonate by the urea organisms present in most soils. The ammonium carbonate is rapidly transformed into nitrous acid and carbonic acid. On the brown silt loam where urea was used without phosphate treatment very curious results were obtained. With wheat, very large increases in growth were evident, more in the unlimed pots than in the limed ones. With sweet clover, urea had practically no effect, while on the yellow silt loam series the effect of urea was small. It is evident that in the brown silt loam the acid production as a result of nitrification resulted in the liberation of a considerable quantity of plant food. The reduction in yield of wheat where lime too was applied lends strength to this statement. The failure of response by sweet clover is the result of toxic effect on the plants by the acids produced. The lesser effect of urea on wheat in yellow silt loam series is due to the poor quality of the soil and the inability of the soil to nitrify the urea as rapidly as the brown silt loam did. There is even a possibility that the urea remained unchanged in the soil long enough to injure the young wheat seedlings. No such injury was visible at any time, however.

#### THE EFFECT OF THE UREA ON THE AVAILABILITY OF THE PHOSPHATES

The effect of the urea on the availability of the phosphates themselves was very remarkable. In many instances yields were almost trebled. Wheat benefited considerably more than sweet clover. The increases in yield due to various treatments are recorded in tables 11, 12, and 13. It is evident that urea exerted its greatest influence on the tricalcium phosphates. Where sweet clover was grown, no, or only small, increases were observed with aluminum phosphates. On the yellow silt loam series, lazulite was the only



aluminum phosphate which benefited by the presence of the urea. An outstanding feature is the remarkable benefit derived by sweet clover from urea and duftenite in the unlimed series, especially as duftenite has proved to be a poor source of phosphorus thus far. The last column on the right of tables 11, 12, and 13 give the increases in yield that may be ascribed as due to the phosphorus alone. It is very doubtful whether the figures can be said to represent the influence of the phosphates because the factors regulating growth are much too intricate to be separated in such an arbitrary fashion; but at the same time they show the percentage increase of growth as due to combined efforts of the urea and phosphates as against the influence of the urea or the calcium nitrate.

Plate 2 shows photographs of the various wheat pots which give a clear picture of the effect of the various treatments. The tremendous increase in growth can only be ascribed to the ability of the urea to render plant food available as a result of its transformation into acids. The small quantity of soil in each pot and hence the relatively small quantity of available plant-food in each pot combined with the large number of plants growing in each pot made it difficult for the plants to grow to any considerable size without the addition of fertilizing materials. The roots made a tangled mass in the soil penetrating into every nook and corner of the pots. Hopkins and Whiting (30) showed that nitrite bacteria could dissolve seven times as much phosphorus from rock phosphate as would be required by a growing plant in a medium where this phosphate was the only supply of a base. The urea was in intimate contact with the phosphorus and, therefore, admirably situated for the acids produced to act on the phosphates, rather than on other soil materials. All the pots were well stocked with nitrogen. It is evident then that in the pots not treated with urea the plants suffered from phosphate starvation, while in the pots treated with urea, phosphorus was dissolved in plenty and the extensive network of roots in the pots ensured the utilization of a large proportion of the phosphorus thus placed at the disposal of the plants. An observation which lends support to this is the fact that the wheat, growing on the urea-treated pots, developed heads and seed, while only in isolated cases did any of the heads develop at all on any of the other pots. Seed production and early maturity are coupled with good phosphorus supply. The depression in yields where lime was used together with urea and phosphate and especially tricalcium phosphates, must be explained as due to the neutralization by the lime of part of the acids formed.

The smaller response to urea by aluminum phosphate is probably due to the fact that aluminum is a questionable base for the nitrifying organisms which are known to respond to calcium and magnesium as bases.

In the sweet clover series the formation of soluble aluminum salts was in all probability detrimental to the plants to which they are known to be very toxic. The difference in yield between check 3 and check 4 in table 12 is large enough to conclude that urea alone had injured the plants but that in the pres-

ence of lime it was beneficial. The results from the sand series bear out the above statements. Urea without lime benefited the wheat by supplying at least some soluble phosphorus; on the limed pots the solvent action of the acids was removed so that the calcium phosphates showed hardly any benefit from the addition of urea, but with the aluminum phosphates the lime rendered the aluminum phosphates available so that but small differences were noticeable. Wheat is not so susceptible to the toxic action of aluminum salts of acidity. In the sweet clover series urea and phosphate without lime caused havoc amongst the plants. All the pots treated with aluminum phosphate had their plants severely injured or killed. Even some pots in limed series suffered. This points strongly in the direction that sweet clover was injured by soluble aluminum salts or by acids, or by ammonium or ammonium nitrite.

#### NITROGEN AND PHOSPHORUS CONTENT WITH AND WITHOUT UREA

The analyses of some of the crops grown in this experiment (table 16) indicate that the differences in growth are due to the supply of available phosphorus rather than to any other causes. The analyses were of wheat grown in the sand series—both nitrogen and phosphorus content were determined.

TABLE 16  
*Analyses of wheat from sand series*

POT NUMBER	TREATMENT	NITROGEN	PHOSPHORUS
		<i>per cent</i>	<i>per cent</i>
111C	Sal., $\text{Ca}(\text{NO}_3)_2$	2.37	0.048
112C	Sal., $\text{Ca}(\text{NO}_3)_2$ , L	2.03	0.054
113C	Sal., urea	2.42	0.076
114C	Sal., urea, L	2.23	0.056
131B	Lgg., $\text{Ca}(\text{NO}_3)_2$	1.96	0.046
132B	Lgg., $\text{Ca}(\text{NO}_3)_2$ , L	2.04	0.047
133B	Lgg., urea	2.12	0.057
134B	Lgg., urea, L	1.95	0.047
141	Bone, $\text{Ca}(\text{NO}_3)_2$	2.01	0.048
142	Bone, $\text{Ca}(\text{NO}_3)_2$ , L	2.02	0.050
143	Bone, urea	2.03	0.059
144	Bone, urea, L	2.03	0.046

phorus rather than to any other causes. The analyses were of wheat grown in the sand series—both nitrogen and phosphorus content were determined.

#### *Experiment 4*

The purpose of this experiment was to determine the availability of chemically pure phosphates of aluminum, iron, and calcium and the effect of ignition on the availability of mineral phosphates of calcium, iron, and aluminum.

In the first part of the experiment, the chemically pure phosphates were compared, with and without the effect of lime, and in order to insure that the calcium phosphate was not placed at a disadvantage by the use of calcium nitrate, comparative pots were planted in which ammonium sulfate was used

as a source of nitrogen. With the aluminum and iron phosphates a small quantity of calcium silicate was added as a source of calcium where ammonium sulfate was used.

TABLE 17

*Yields of buckwheat on pots with chemically pure phosphates and ignited mineral phosphates*

POT NUMBER	TREATMENT IN ADDITION TO NUTRIENT SOLUTION	WEIGHT OF CROP		
		First pot	Second pot	Average
		gm.	gm.	gm.
1	Al. P., $(\text{NH}_4)_2\text{SO}_4, \text{CaSiO}_3$	3.00	3.30	3.15
2	Al. P., $(\text{NH}_4)_2\text{SO}_4, \text{L}, \text{CaSiO}_3$	4.67	4.64	4.66
3	Al. P., $\text{Ca}(\text{NO}_3)_2$	6.20	6.63	6.42
4	Al. P., $\text{Ca}(\text{NO}_3)_2, \text{L}$	6.92	7.00	6.96
11	Fe. P., $(\text{NH}_4)_2\text{SO}_4, \text{CaSiO}_3$	4.47	4.55	4.51
12	Fe. P., $(\text{NH}_4)_2\text{SO}_4, \text{L}, \text{CaSiO}_3$	4.71	4.35	4.53
13	Fe. P., $\text{Ca}(\text{NO}_3)_2$	5.39	6.20	5.80
14	Fe. P., $\text{Ca}(\text{NO}_3)_2, \text{L}$	6.27	5.67	5.97
21	Ca. P., $(\text{NH}_4)_2\text{SO}_4$	4.31	4.25	4.28
22	Ca. P., $(\text{NH}_4)_2\text{SO}_4, \text{L}$	3.16	3.18	3.17
23	Ca. P., $\text{Ca}(\text{NO}_3)_2$	6.65	6.92	6.79
24	Ca. P., $\text{Ca}(\text{NO}_3)_2, \text{L}$	4.51	4.83	4.67
31	Laz. I., $\text{Ca}(\text{NO}_3)_2$	3.33	3.65	3.49
32	Laz. I., $\text{Ca}(\text{NO}_3)_2, \text{L}$	4.76	4.70	4.73
33	Laz., $\text{Ca}(\text{NO}_3)_2$	1.56	1.40	1.48
34	Laz., $\text{Ca}(\text{NO}_3)_2, \text{L}$	2.14	2.57	2.36
41	Wav. I., $\text{Ca}(\text{NO}_3)_2$	5.96	5.87	5.92
42	Wav. I., $\text{Ca}(\text{NO}_3)_2, \text{L}$	7.49	8.05	7.77
43	Wav., $\text{Ca}(\text{NO}_3)_2$	2.80	2.47	2.64
44	Wav., $\text{Ca}(\text{NO}_3)_2, \text{L}$	3.59	3.18	3.39
51	Sal. I., $\text{Ca}(\text{NO}_3)_2$	5.93	6.06	6.00
52	Sal. I., $\text{Ca}(\text{NO}_3)_2, \text{L}$	7.89	7.87	7.88
53	Sal., $\text{Ca}(\text{NO}_3)_2$	3.03	3.50	3.27
54	Sal., $\text{Ca}(\text{NO}_3)_2, \text{L}$	4.95	4.04	4.50
61	Duf. I., $\text{Ca}(\text{NO}_3)_2$	2.24	2.29	2.27
62	Duf. I., $\text{Ca}(\text{NO}_3)_2, \text{L}$	2.00	2.29	2.15
63	Duf., $\text{Ca}(\text{NO}_3)_2$	1.40	1.86	1.63
64	Duf., $\text{Ca}(\text{NO}_3)_2, \text{L}$	1.60	1.76	1.68
71	Fl. R. I., $\text{Ca}(\text{NO}_3)_2$	6.31	5.96	6.14
72	Fl. R. I., $\text{Ca}(\text{NO}_3)_2, \text{L}$	4.80	4.56	4.68
73	Fl. R., $\text{Ca}(\text{NO}_3)_2$	6.11	6.21	6.16
74	Fl. R., $\text{Ca}(\text{NO}_3)_2, \text{L}$	4.48	4.77	4.63

\* Key to Abbreviations: Al. P., Aluminum phosphate; Fe. P., pure ferric phosphate; L., ignited.

The medium used was pure quartz sand which received the same nutrient solution at the same intervals as described in experiment 3. The limestone and other salts were applied in the same manner and quantities as in the former experiments.

These pots were planted on January 17, 1920, and harvested March 29. On three separate occasions the plants were dusted with tobacco dust to control the thrips with which they had become infested. The buckwheat plants were thinned until 6 remained in each pot.

The crops, when harvested, were placed in paper bags, dried in an oven at 105°C., and weighed. Table 17 gives the weights of crops obtained.

#### DISCUSSION AND RESULTS OF EXPERIMENT 4

The weights of crops obtained are well in accord with what one might expect from the results of experiment 1. Calcium nitrate is evidently a far better form of nitrogen for buckwheat than is ammonium sulfate. Even with calcium phosphate, calcium nitrate proved to be the better form of nitrogen in spite of the fact that ammonium sulfate is supposed to enhance the assimilability of tricalcium phosphates. It is fortunate that calcium nitrate was chosen for the latter half of the experiment as a source of nitrogen. Of the pure phosphates, we may safely state aluminum phosphate is as available as calcium phosphate and that these two are only slightly superior to ferric phosphate as a source of phosphorus for buckwheat. The effect of lime on the availability of the pure aluminum phosphate was not so much in evidence as it was with the mineral phosphates of aluminum. This is to be expected. The aluminum phosphate is free to hydrolyze readily at the beginning, having no aluminum hydrate associated with it. Only as time goes on and the aluminum hydrate begins to accumulate does the lime exert its influence on the availability of the phosphates. With iron and calcium phosphates the effect of lime resulted as expected. The slight effect of lime on pure aluminum phosphate, the failure to affect ferric phosphate at all and the great depression in availability of pure tricalcium phosphate is cited again as strong evidence in support of the theory described under the first experiment as to the effect of lime on the availability of aluminum, iron, and calcium phosphates.

In connection with the relative availabilities of the three types of phosphates to crops, it must be borne in mind that a plant with great ability to utilize tricalcium phosphate was employed, as has been demonstrated time and again. It is very probable that had wheat, oats, millet, flax, or some such low-feeding-power plant been used instead of buckwheat, aluminum and iron phosphates would have shown up to better advantage since their phosphorus is rendered available more readily by hydrolysis than by the action of roots through the agency of carbonic acid. Acids have less solvent action on aluminum and iron phosphates than on calcium phosphates as has been demonstrated in experiment 3.

Ignition of the phosphates has had a remarkable effect on the assimilability of the phosphorus. It may be stated here that the phosphates were ignited at a bright red heat for 5 hours. Saldanha phosphate and wavellite lost about 15 per cent of their weight; the other three phosphates about 5

per cent. This loss of weight was, of course, taken into account when applying the phosphates so that all phosphates were applied on an equal phosphorus basis. Ignition of the three aluminum phosphate minerals resulted in doubling the crops obtained with them as compared with the unignited minerals. Smaller but still significant increases in yields were realized by igniting dufrénite. Ignition has had no influence on the availability of the calcium phosphate used.

The increased availability of the aluminum and iron phosphates may be due to two causes:

1. Dehydration of the mineral and dehydration of the aluminum and ferric hydrates associated with the phosphate.

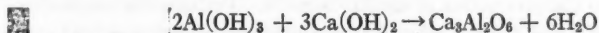
2. Destruction of the physical structure of the minerals. The first cause seems to be the more logical one. As has been explained in experiment 1, the basic phosphates are less available than the non-basic ones. With the lazulite, wavellite, and Saldanha phosphates we have associated a quantity of aluminum hydrate. Ignition converts the hydrates into oxides:



With dufrénite we have associated ferric hydrate which is dehydrated:



Now aluminum and ferric oxides are far less soluble than aluminum and ferric hydroxides, so that they would, therefore, exert a less depressing effect on the availability of the phosphates. No doubt these oxides will slowly again be converted into hydrates in the soil, but this hydration is slow and furthermore in the case of aluminum hydrate, as hydration proceeds, the lime will precipitate the aluminum as calcium aluminate.



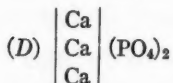
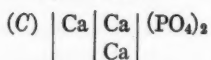
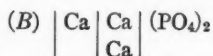
This precipitation will also be more effective than when the lime has to act on the aluminum hydrate en masse. The inability of lime to remove the ferric hydrate explains the smaller effect of ignition on the availability of the dufrénite.

In the unlimed pots treated with ignited aluminum phosphate and in all the pots treated with ferric phosphate, the process of hydration of the oxides is gradual so that most of the alumina and ferric oxide will at first occur as partially hydrated oxides:  $\text{AlO}(\text{OH})$ ,  $\text{Al}_2\text{O}(\text{OH})_4$ ,  $\text{FeO}(\text{OH})$ ,  $\text{Fe}_2\text{O}(\text{OH})_4$ , and numerous others. These partially hydrated oxides are not as soluble as the fully hydrated ones and would therefore exert less influence on the solubility of the phosphates, their hydrolysis, and final assimilation by the plants.

The destruction of physical structure of the minerals may, of course, be an important consideration. The solubility of the minerals may readily be greatly altered by destruction of the crystalline structure. The natural

solubility of the minerals will greatly affect the rate of hydrolysis of the various minerals. There are large possibilities for accounting for many riddles with regard to phosphates on the basis of crystalline structure of the minerals.

Quartaroli (63) claims the existence of two dicalcic phosphates which he represents schematically by  $\text{Ca}/\text{Ca}/(\text{HPO}_4)_2$ , and  $\begin{array}{c} \text{Ca} \\ | \\ \text{Ca} \end{array} | (\text{HPO}_4)_2$ . The first is amorphous and transformable into  $\text{Ca}(\text{H}_2\text{PO}_4)_2$  and the second is crystalline and not transformable into  $\text{Ca}(\text{H}_2\text{PO}_4)_2$ . He suggests the possibility of four forms of tricalcium phosphates which he represents schematically as:



(A) would be gradually transformable into dicalcium phosphate, then monocalcium and finally into phosphoric acid; (B) would be transformable into the crystalline type of dicalcium phosphate and would not be able to produce any monocalcium phosphate; (C) would pass from tricalcium phosphate to the monocalcium phosphate without yielding the dicalcium phosphate and finally form phosphoric acid; (D) cannot be converted into di- or monocalcium phosphate but passes directly to phosphoric acid. Quartaroli has proven the presence of two lithium phosphates. He claims that phosphorites are mixtures of the four forms of calcium phosphate. Aluminum and iron phosphates would lend themselves to the production of similar isomers. Perhaps the variability inter se in availability of calcium phosphates, aluminum phosphates, and iron phosphates is due to the varying proportions of the different isomers in the several minerals. Ignition may or may not alter the proportions of the various isomers and so exert its effect on the availability of the various phosphates. The differences in the availability of lazulite, wavellite, and Saldanha phosphates, that of Florida rock and Laingsburg phosphate, etc., may easily be due to the proportions of the various possible isomers as suggested by Quartaroli.

It is very remarkable that ignited wavellite and Saldanha phosphates on the limed pots should have produced larger crops than even any of the pure phosphates. The availability of lazulite was much increased as a result of the ignition but in no form did the lazulite prove nearly as good as wavellite or Saldanha phosphates. This proves that there is a fundamental difference between the aluminum phosphates in these three minerals. Neither the crystalline structure nor the presence of aluminum hydrate can be designated



as the reason. It seems that Quartaroli has made a very notable contribution to our understanding of the phosphates we deal with in agriculture.

Plate 3, figure 2, shows the relative growth made by the buckwheat with the ignited and unignited aluminum phosphate minerals.

#### *Experiment 5*

In this experiment an attempt was made to illustrate some factors, which affect the availability of phosphates.

The first factor studied was the solubility of aluminum phosphate in an alkaline solution. The plan followed was similar to that of Kossovitch (37) described on page 356 in the survey of literature. Three pots were planted. Inside each pot there was placed a porous pot made of bauxite. The porous pot had the same depth as the gallon pots used throughout this experiment and had a diameter of about 4 inches. This pot allowed the penetration of crystalloids in solution but effectively withstood root penetration through its walls.

In pot 1, both the inner and the outer pots were filled with sand. The outer pot received an application of lime and ferric chloride. The rest of the plant-food materials were applied in a nutrient solution containing monocalcium phosphate, potassium sulfate, and magnesium sulfate.

In pot 2, the inner pot received an application of 10 gm. of wavellite well mixed with the sand and the outer pot, an application of lime and ferric chloride. The rest of the plant nutrients were added in the form of a nutrient solution containing potassium sulfate, magnesium sulfate, and potassium carbonate.

The nutrients were all applied in the manner and amounts already described, except that one-third of the potassium sulfate was replaced by an equivalent in potassium of potassium carbonate.

In pot 3, was a duplicate of pot 2, except that the wavellite was applied in the outer pot instead of the inner pot.

Inoculated annual white sweet clover seed was sowed in the outer pots. All the pots were planted in duplicate. The nutrient solutions were applied only through the inner pot. All the water added was applied to the inner pot, so that the soil solutions reaching the plant roots all passed through the walls of the porous pot. Planting occurred on March 23, 1920, harvesting on May 27, 1920.

During the first month of the growing period, it was not thought that the plants in pot 2 would survive. On pot 1, the sweet clover grew luxuriantly. On pot 3, fairly good growth was obtained. At the end of the month the plants in pot 2 suddenly began growing, those near the porous pot first, those farther away in succession until all the plants were growing. Ten plants were finally left in each pot. The yields are given in table 18.

Enough growth was obtained on pot 2 to give confidence that the plants obtained phosphorus. Thus, phosphorus must have been dissolved by the

nutrient solution and diffused through the walls of the porous pots. In alkaline soils, then, aluminum phosphate will be dissolved by the soil solution. This fact is in accord with Storer's statement (73). Plate 4, figure 1, shows a photograph of the roots of the plants clustered around the porous pots. Chemotaxis is probably the cause for the location of the roots of the plants.

The second factor studied was the solvent effect of plant roots on various phosphates.

Thin, flat, smooth-surfaced plates of plaster of Paris were made. While the plaster was setting, phosphate was dusted onto one surface through a 200-mesh sieve and smoothed over the surface, so that the entire surface was covered with a thin uniform layer of phosphate which was also firm and smooth. All portions of the plates not covered with phosphate were carefully painted with "asphaltum" paint. With a little practice very satisfactory smooth phosphate surfaces may be produced. Such plates were made using Saldanha

TABLE 18  
*Yields of sweet clover*

POT NUMBER	WEIGHT OF CROPS		
	First pot	Second pot	Average
	gm.	gm.	gm.
1	14.25	13.62	13.94
2	3.27	2.67	2.97
3	7.87	8.7	8.31

phosphate, wavellite and Laingsburg phosphate. Each plate was placed vertically in a pot of sand moistened with a nutrient solution containing potassium sulfate, magnesium sulfate, and ferric chloride in the proportions already described in former experiments. The sand also received an application of limestone and gypsum, the latter at the rate of 200 pounds per acre. There were two plates of each phosphate. In the one case, a sweet clover plant about 6 inches tall was placed with its roots against the phosphate surface, in the other the plant was set on the side opposite to which the phosphate was to be found. Eight weeks after planting, the plants were removed from the pots and the roots and the plates examined. Plates 4 and 5, accurately depict the effect of the plant roots on the phosphate surfaces. The roots of the plants were matted all over the surface of the phosphate, a large portion of which had been removed. The pitted appearance of the plates marked clearly the corrosive effect of the roots.

The sweet clover plants using calcium phosphate developed slightly better than the other four plants but the use of only one plant precludes the drawing of any conclusions as to the best phosphate in this form.

The plant roots could find phosphate only in very limited area. Nearly all the roots were confined to that area. The demonstration, while giving no actual proof, indicates that root contact with the insoluble phosphates is important as a factor in the assimilation of such phosphorus and that roots of sweet clover have considerable ability in rendering phosphates soluble, probably as a result of acid excretion. It was noticeable that the roots growing against the phosphate plates were considerably flattened.

#### GENERAL DISCUSSION

The phosphorus of the soil occurs in the form of organic compounds and minerals; the latter chiefly as aluminum, calcium, iron, and magnesium phosphates. These mineral phosphates may of course be in the form of complexes with organic matter as suggested by Peterson (51), especially if the phosphates are basic ones. Acid humic bodies and acid silicates may readily form compounds with basic phosphates. Truog (77) points out that these compounds may be "very resistant and insoluble compounds."

It is the problem of agriculturists to furnish growing crops a plentiful supply of phosphorus to be drawn from the stock in the soil. Each of the various phosphorus-containing compounds has a different degree of availability and, what is perhaps more important, demands certain special conditions for its maximum availability which vary with each type of phosphate. The ideal practice for the farmer is to obtain such conditions as will yield him the largest quantity of available phosphorus per acre. In order to prevent the deterioration of the land, this involves maintaining and generally, too, increasing the stock of phosphorus in his soil. The necessity of growing and plowing under legumes to add nitrogen to the soil involves almost invariably the use of limestone. Few legumes thrive in acid soils. Apart from the question of growing legumes it is a known fact that the organisms involved in transforming organic nitrogen into the nitrate form thrive best on calcareous media. Centuries of profitable employment of lime is proof enough of the value and the necessity of its use. Drainage, cultivation, liming, and incorporation of organic matter with the soil are essential farm practices on most of the arable soils of the world. These practices must be followed. The kind and amount of phosphorus compounds to be applied, the time and manner of application, the kind of crops grown, the use of catch crops, the employment of other fertilizers not involving phosphorus are the factors which the farmer may use in order to make the best use of the phosphorus of the soil and of insuring a good supply of phosphorus to the crops he grows.

The investigations reported in this paper have shown that plants can utilize aluminum, iron, and calcium phosphates to some extent. Certain forms of each of these phosphates are better than others; certain conditions improve, other conditions impair, the availability of these phosphates. Under all conditions, however, plants are able to obtain some phosphorus from any of the minerals used. The greater the stock of phosphorus in the soil, then the

greater the amount the plants can obtain. The greater amount of surface exposed to agencies tending to dissolve the phosphorus, and the greater amount of contact of phosphate with the plant roots are two favorable factors which would multiply the effectiveness of the extra phosphate.

Insuring the presence of a large quantity of phosphorus in the soil is the solution of the fundamental soil problem. Hopkins (29) claims that good farming practice renders 1 per cent of the phosphorus in the surface layer available every year. Twenty-three hundred pounds of phosphorus per acre would insure the availability of sufficient phosphorus to produce maximum crops of such plants as corn, oats, alfalfa, wheat, etc. If Hopkins' claim is true, the first step in the solution of the phosphorus problem of the soil would be to raise the phosphate stock of the soil to the above amount.

The choice of the type of phosphorus to add is the second problem. The experiments reported above would indicate that as an average, calcium phosphates are to be preferred. In a soil well stocked with limestone, however, aluminum phosphates may be more desirable. There is no doubt that very satisfactory results may be obtained by the use of aluminum phosphate. The price of the material would be the big factor in determining the choice of phosphates. Aluminum phosphates should never be used on acid soils unless, of course, lime is applied at the same time. In fact it would be preferable to apply lime together with the aluminum phosphate so that the two may be in intimate contact in the soil. Tricalcium phosphates are used with greater effect on acid soils. Iron phosphates have a doubtful value. If the phosphate is not basic it may be applied to advantage but the lasting effects will be much lower than that for calcium phosphates or aluminum phosphates on limed soils. In choosing phosphates to apply to soil, discretion should be used. No phosphate material should be used without a preliminary test. The low assimilability of the phosphorus in dufrenite and lazulite is a warning against indiscriminate buying of these phosphates.

Aluminum, iron, and calcium phosphates vary as to the manner in which they are rendered available in the soil. It would perhaps be a good policy to apply both aluminum and calcium phosphates to the soil so as to make full use of all the reactions which tend to place phosphorus at the disposal of plants.

Considering the time of applying phosphorus, it would be wise to apply phosphorus for the green-manuring crop especially if clover, sweet clover, rape, mustard, or some such heavy feeder on phosphorus is used. These crops will then place the phosphorus they have used at the disposal of the money crops following. This practice would be especially desirable where aluminum phosphates are used. With calcium phosphates, it would perhaps be more desirable to plow the phosphate into the soil with the green-manuring crop in order to utilize to the fullest extent the acids produced during nitrification of the nitrogenous material and at the same time placing the phosphorus in intimate contact with the big source of carbonic acid production. The urea experiment reported above is further support of the results of Hopkins and

Whiting (30) regarding the effect of nitrification on the availability of phosphates.

Truog (77) makes a suggestion for a rotation of crops in Wisconsin in which he introduces white mustard and rape as catch crops, the former being planted after wheat harvest, the latter, the following year in corn at the last cultivation. The third year clover is seeded in the oats, the fourth year the field remains in clover. This suggestion is an admirable one in the direction of keeping the soil well supplied with organic matter and in using other crops to help the weak feeding *Graminae* to obtain readily available phosphorus.

Acid phosphate and soluble phosphates, in general, are usually too expensive to have a place in building up the phosphorus stock of a soil. They can be used with effect in another direction. If small top dressings of this phosphate be used, they will serve to give the young seedlings a rapid start so that they will develop a strong root system which will then function in feeding the plant in later growth stages. This practice should be used only in connection with a system in which adequate provision is made for stocking the soil with phosphorus. If not, the practice will prove to be one of the best ways of rendering a poor soil poorer.

#### CONCLUSIONS

1. Mineral phosphates of aluminum and iron are valuable sources of phosphorus for plants; under certain conditions they are superior to calcium phosphate, under others inferior.

2. Nitrification of urea with the consequent production of acids acts very favorably in assisting plants to obtain phosphates of aluminum, iron, and calcium for food.

3. Chemically pure phosphates of aluminum and iron are as readily available to the plants tested as is pure calcium phosphate.

4. Mineral phosphates of aluminum and iron are not as readily available as the pure phosphates of the same metals due to the fact that most of them are hydrated basic phosphates.

5. Igniting the minerals, thereby dehydrating the bases associated with the phosphates and destroying the crystalline structures of the minerals, removes the drawback against the use of mineral phosphates of aluminum and iron.

6. Aluminum phosphates, whether chemically pure or in mineral form, ignited or unignited, always display their maximum effect in a calcareous medium.

7. The effect of iron phosphates is neither enhanced nor depressed by the addition of limestone under the conditions of the experiment.

8. Under the conditions of the experiments, where chiefly neutral growing media were used, tricalcium phosphates were affected adversely by the addition of limestone.

9. An alkaline soil solution dissolves aluminum phosphate and aids the plant in obtaining its phosphorus for food.

10. Contact of the roots of plants with mineral phosphates is a very important factor in the assimilation of the phosphorus by plants for food.

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## PLATE 1

Fig. 1. Buckwheat six weeks old in sand culture.

Pot number	Treatment	Pot number	Treatment
1201A....	Lazulite	1201C....	Saldanha
1202A....	Lazulite and lime	1202C....	Saldanha and lime
1203A....	Lazulite and gypsum	1203C....	Saldanha and gypsum
1204A....	Lazulite, lime and gypsum	1204C....	Saldanha, gypsum and lime
1301A....	Dufrenite	1201B....	Wavellite
1302A....	Dufrenite and lime	1202B....	Wavellite and lime
1303A....	Dufrenite and gypsum	1203B....	Wavellite and gypsum
1304A....	Dufrenite, lime and gypsum	1204B....	Wavellite, gypsum and lime

Fig. 2. Sweet clover six weeks old in sand cultures showing effect of lime

Pot number	Treatment	Pot number	Treatment
x1705.....	Mono calcium phosphate	x1402B....	Laingsburg phosphate and lime
x1202C....	Saldanah phosphate and lime	x1401B...	Laingsburg phosphate alone
x1201C....	Saldanah phosphate alone	x1402A...	Florida Rock phosphate and lime
x1202B....	Wavellite and lime	x1401A...	Florida Rock phosphate alone
x1201B....	Wavellite alone	x1601....	Bonemeal and lime
x1302B....	Vivianite and lime	x1602B...	Bonemeal alone

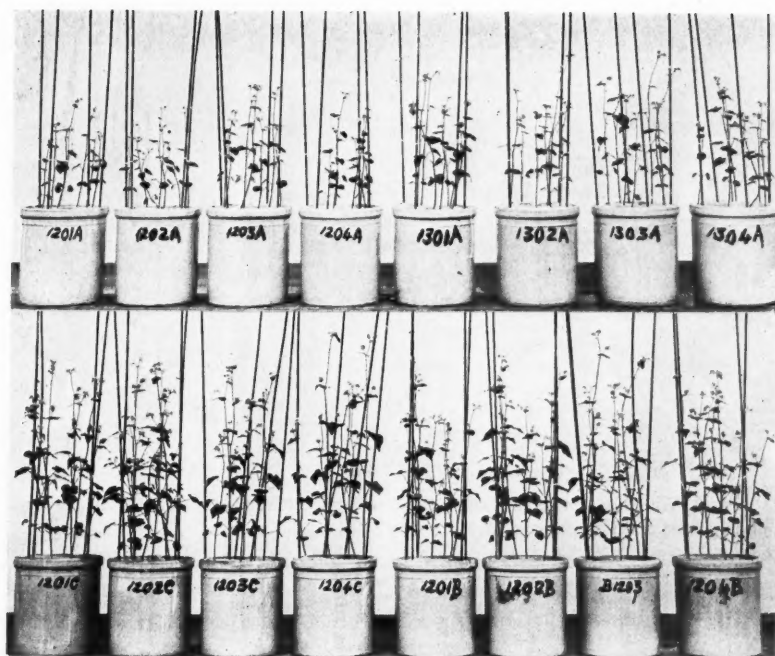


FIG. 1.

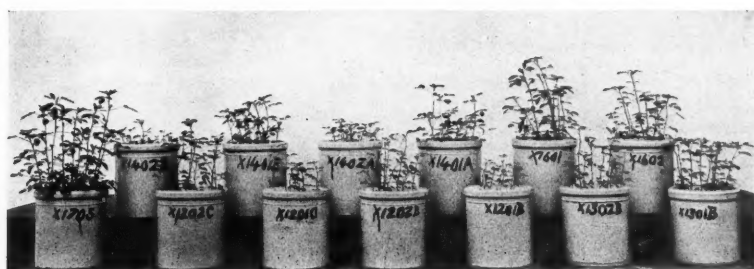


FIG. 2.

PLATE 2

FIG. 1. Wheat on brown silt loam series showing the effect of urea on the availability of aluminum and iron phosphates.

FIG. 2. Wheat on yellow silt loam series showing the effect of urea on the availability of the calcium phosphates.



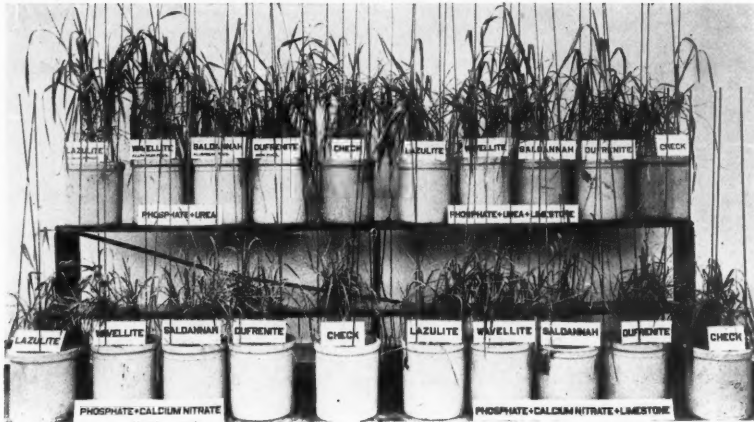


FIG. 1.

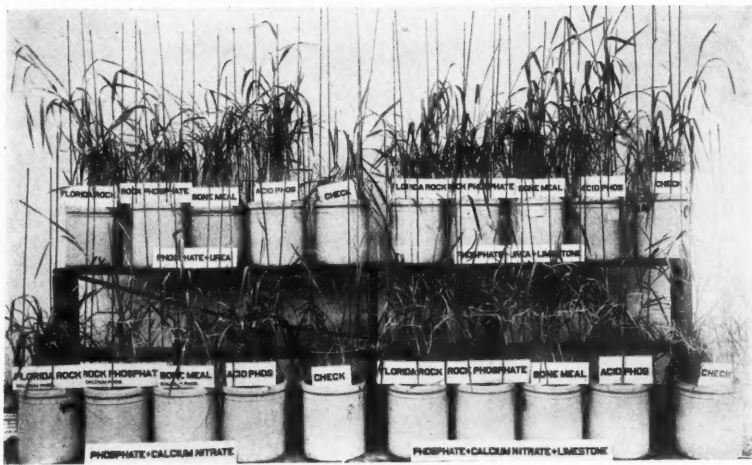


FIG. 2.

PLATE 3

FIG. 1. Wheat and clover in sand series showing the best pot with each of various phosphates.

FIG. 2. Buckwheat on sand culture showing effect of ignition on availability of aluminum phosphates.

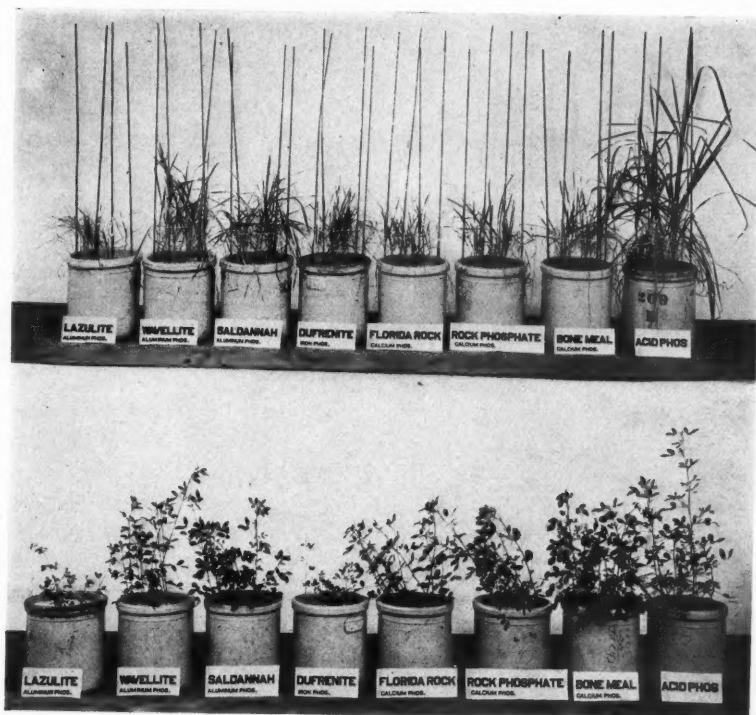


FIG. 1.



FIG. 2.  
405

UN

PLATE 4

FIG. 1. Roots of sweet clover clinging to the porous pots. Pot on right received soluble phosphorus.

FIG. 2. Effect of sweet clover roots on smooth surface of wavellite.

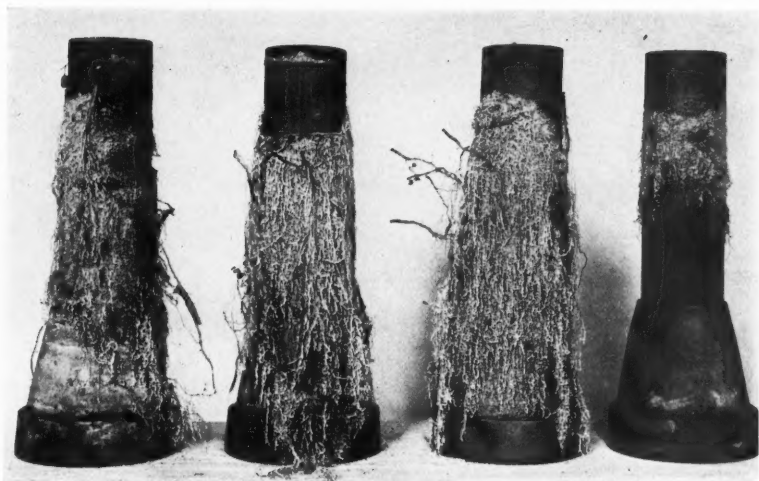


FIG. 1.



FIG. 2.

PLATE 5

FIG. 1. Effect of sweet clover on smooth surface of Laingsburg phosphate (rock phosphate).

FIG. 2. Effect of sweet clover on smooth surface of Saldanah phosphate.





FIG. 1.



FIG. 2.

